ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

INVESTIGATION OF THE EFFECTS OF CHROME-TANNED LEATHER ADDITIVES IN ETHYLENE PROPYLENE DIENE MONOMER RUBBER

M.Sc. THESIS

Pınar MEŞE

Department of Polymer Science and Technology

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Thesis Advisor: Prof. Dr. Nurseli UYANIK

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KROMLA TABAKLANMIŞ DERİ KATKISININ ETİLEN PROPİLEN DİEN MONOMER KAUÇUĞUNA ETKİSİNİN İNCELENMESİ

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To my family,

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May 2014 Pınar MEŞE

Chemical Engineer

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ABBREVIATIONS

EPDM	**:** Ethylene Propylene Diene Monomer
CTL	**:** Chrome Tanned Leather
NR	**:** Natural Rubber
SBR	**:** Styrene-Butadiene Rubber
NBR	**:** Acrylonitrile-Butadiene Rubber
BR	**:** Polybutadiene
IR	**:** Polyisoprene
IIR	**:** Butyl Rubber
BIIR	**:** Brominated Butyl Rubber
CIIR	**:** Chlorinated Butyl Rubber
CR	**:** Polychloroprene Rubber
CB	**:** Carbon Black
ZnO	**:** Zinc Oxide
IPPD	**:** N-Isopropyl-N'-Phenyl-p-Phenylene-Diamine
TMQ	**:** 2, 2, 4-Trimethyl-1,2-Dihydroquinoline
TMTD	**:** Tetramethlythiuram Disulfide
MBT	**:** 2-Mercaptobenzothiazole
DSC	**:** Differential Scanning Calorimeter
T_g	**:** Glass Trasition Temperature
ΔH_c	**:** Curing Peak Enthalpies
MDR	**:** Moving Die Rheometer
ISO	**:** International Organization for Standardization
TGA	**:** Thermogravimetric Analysis
M_H	**:** Maximum Torque
M_L	**:** Minimum Torque
ts_2	**:** Scorch Time
t_{10}	**:** Time to Reach 10% of Maximum Torque
t_{50}	**:** Time to Reach 50% of Maximum Torque
t_{90}	**:** Time to Reach 90% of Maximum Torque
t_{100}	**:** Time to Reach 100% of Maximum Torque
CRI	**:** Cure Rate Index
CLD	**:** Crosslinking Density
PHR	**:** Per Hundred Rubber
MPa	**:** Mega Pascal

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INVESTIGATION OF THE EFFECTS OF CHROME-TANNED LEATHER ADDITIVES IN ETHYLENE PROPYLENE DIENE MONOMER RUBBER

SUMMARY

Rubbers are in general not used in their pure form but are reinforced with fillers can be very strong. The addition of filler changes the properties of rubber significantly. The reinforcement of rubber is done to increase of mechanical properties, reduce cost, improve processability especially. Ethylene propylene diene monomer (EPDM) is one of the most important synthetic rubber. EPDM shows high mechanical and electrical properties, good resistance to aging, heat and low temperature flexibility. It has an ability to accept high load fillers, reinforcing materials or plasticizers. Mostly used additives to rubber are fillers, reinforcing fillers, activators, curing agents, accelerators etc. Leather is consisting of collagen and keratin fibers. The collagen structure of skin must be stabilized with tanning process to aviod its degradation. Chrome tanning process of leather is the most widely used technique by the leather industry. The conventional leather tanning results improved in physical& chemical properties and appearance. Approximately, 90% of tanning process is carried out with chromium III salts.

In this study, chrome tanned leather (CTL) particles were incorporated into EPDM rubber to investigate the curing, thermal, mechanical and morphological properties before and after thermal aging at 70 °C and 70 hours. CTL shavings were cutted into smaller pieces before adding to mix and then dried in an oven 100 °C during 24 hours due to remove the moisture. From sieve analyser, mesh size percentages were measured between 45 to 2000 µm and the most used particle size (36.6 wt.-%) was 1000 µm. CTL particles were mixed with zinc oxide (ZnO) and waited during one day.

CTL were added in EPDM rubber with different ratios. EPDM/CTL compounds were prepared firstly by using laboratory type banbury mixer and then two roll mill by adding 0 to 20 phr CTL. Differential scanning calorimeter (DSC) was used to determine the glass transition temperature (T_g) and curing peak enthalpies (ΔH_c) at 160 °C temperature. T_g values decreased and ΔH_c values increased with loading CTL into EPDM. Video microscope was used to examine the surface properties of compounds. Brightness increased with CTL loading. Curing properties of compounds obtained using moving die rheometer (MDR) at 160 °C temperature. Scorch time (t_{s2}) , optimum cure time (t_{90}) , minimum (M_L) and maximum torque (M_H) values were recorded. Curing times differs from 11 to 21 minutes. M_L and $M_H$values decreased as we compare with EPDM rubber. Densities were measured to calculate the mass of compounds which will be vulcanized in hot press at 160 °C. Samples were prepared 2 mm thickness sheets. Mechanical properties such as tensile and tear strength, elongation at break, 50% secant modulus of samples were recorded after vulcanization process using universal testing machine. Hardness was measured using Shore A type durometer. Tensile strength andelongation at break values decreased while secant modulus values showed no significant change. Crosslinking densities of EPDM/CTL samples are determined with 50% secant modulus which are

obtained from tensile test. Hardness values increased with CTL loading. Tear strength values showed good increase with adding CTL particles from 0 to 20 phr. This increase showed the effectively prevents the growth of test samples crack.

Thermogravimetric analysis (TGA) was used to determine the degradation and mass loss of ingredients. First mass loss between 320-350 ℃ is due to oil in the structure, second mass loss is between 450-470 ℃ is due to rubber degradation and third mass loss is between 670-690 °C is due to carbon black. Little amount of inorganic filler stayed after 750 ℃ temperature.

Different formulation sheets which are 2 mm thickness were subjected to thermal aging at 70 °C and 70 hours. After aging mechanical properties were investigated. Tensile and tear strength, elongation at break, 50% secant modulus of samples were recorded by universal testing machine. After aging, modulus values increased significantly when it was compared with before aging properties. Tensile strength and elongation at break values did not show significant change with aging. Although there was not significant changes in the 50% secant modulus similarly, a small increase observed after aging. EPDM is resistant to thermal aging and with addition of leather in EPDM showed resistance to heat similar to EPDM rubber. Tear strength decreased small amount with CTL loading from 0 to 20 phr after aging. Hardness values were also measured after aging and it was found that an increase with CTL loading from 0 to 20 phr after aging than those of before aging results. 6 mm thickness and 50 mm diameter samples were prepared at 160 °C for compression set test for each different formulations. Samples were compressed by 25% of its original thickness during 70 °C and 70 hours. Although compression set values showed no significant change, it indicated a decrease. Compressability properties of EPDM/CTL rubbers were increased as compared with EPDM rubber.

KROMLA TABAKLANMIŞ DERİ KATKISININ ETİLEN PROPİLEN DİEN MONOMER KAUÇUĞUNA ETKİSİNİN İNCELENMESİ

ÖZET

Kauçuklar, yüksek esneklik, yüksek dayanım, düşük deformasyon, kolay işlenme, iyi yırtılma ve aşınma dayanımı gibi özellikleri sebebiyle çok geniş bir kullanım alanı olan polimer sınıfındandır. Kauçuklar, uygulanan kuvvetin kaldırılmasıyla orijinal boylarına geri dönebilen malzemeler olarak tanımlanmıştır. Bu malzemeler çapraz bağlanmamış ama çapraz bağlanabilme özelliğine sahip, yani vulkanize olabilen polimerlerdir. Vulkanizasyon , kauçuğu kükürtle ısıtma işlemi ve bu işlemde polimer zincirlerinin kükürt atomları aracılığı ile çapraz bağlanmasıdır. Bu çapraz bağlar kauçuğa direnç verir ve kauçuğun elastik davranış sergilemesini sağlar. Kauçuklar, doğal ve sentetik kauçuk olarak ikiye ayrılırlar. Başlıca sentetik kauçuklar; stiren bütadien kauçuk, etilen propilen dien kauçuk, poliisopren kauçuk, akrilonitril bütadien kauçuk, neopren ve silikon kauçuktur. Etilen propilen dien monomer (EPDM) en önemli sentetik kauçuklardan biridir. Yapısında çift bağ bulunduğundan doymuş yapıda olan EPDM kauçuğu diğer polimerlerle karışabilmekte, kükürt ve ısıyla birlikte vulkanize olabilmektedir. Yüksek derecede dolgu maddesi, takviye elemanı veya plastikleştirici ile karışabilme yeteneği vardır. EPDM, yüksek mekanik ve elektriksel özellik, yaşlandırmaya, ısıya ve düşük sıcaklık elastikiyeti gibi özelliklere sahiptir. Bu özelliklerinden dolayı otomotiv endüstrisi bu kauçuğun önemli bir payını oluşturmaktadır.

Kauçuklar genelde saf halde kullanılmayıp dolgu maddesi eklenerek kullanıldığında çok sağlam malzemeler haline gelirler. Dolgu maddelerinin eklenmesi kauçuk özelliklerini önemli derecede değiştirir. Katkı maddelerinin eklenmesiyle, mekanik özelliklerin iyileşmesi, fiyatın düşmesi, iyi işlenebilme gibi özelliklerde artış gözlenir. Kauçuklara en çok eklenen katkı maddeleri; dolgu maddeleri, takviye elemanı, aktivatörler, kürleşme ajanları veya sülfür gibi hızlandırıcılardır. Deri maddesi yapısında kollajen, keratin ve yağ bulundurur. Derinin kollajen yapısı, bozunmayı önlemek için yapılan kromla tabaklama prosesiyle kararlı hale gelir. Kromla tabaklama prosesi, deri endüstrisinde en çok kullanılan yöntemdir. Geleneksel deri tabaklama işleminde fiziksel ve kimyasal özellikleri yükselirken ve görünüşünde de iyileşme meydana gelir. Yaklaşık olarak, kromla tabaklama prosesinin % 90'ı krom III tuzları ile gerçekleşir.

Bu çalışmada, kromla tabaklanmış deri (CTL) parçacıkları, EPDM kauçuğuna katılarak, yaşlandırma öncesi ve 70 °C 'de 70 saat yaşlandırıldıktan sonra mekanik, ısıl özellikleri incelendi. CTL lifleri karışıma eklenmeden önce küçük parçalar şeklinde kesildi ve yüksek nem içeren yapısından dolayı, nemi uzaklaştırmak için 100 °C'de 24 saat boyunca etüvde beklendi. Elek analizi yöntemiyle, kullanılan deri parçacıklarının boyutu 45 ile 2000 µm arasında ölçüldü. En fazla kullanılan parçacık boyutu (36.6 ağ.-%) 1000 µm olarak kaydedildi. CTL parçacıkları çinko oksit ile karıştırılarak 1 gün boyunca beklendi.

CTL katkısının EPDM kauçuğuna etkisini incelemek için değişik oranlarda karışımlar hazırlandı. EPDM/CTL karışımlarının hamurları 0-20 phr aralığında eklenerek öncelikle laboratuvar tipi banbury karıştırıcısında, daha sonra da kauçuk milinde hazırlanmıştır. 160°C sıcaklıkta diferansiyel taramalı kalorimetre (DSC) ile hamurların camsı geçiş sıcaklıkları (T_g) ve kürleşme pik entalpileri (ΔH_c) elde edilmiştir. EPDM kauçuğuna deri parçacıklarının eklenmesiyle T_g değerleri düşerek ΔH_c değerleri artış göstermiştir. Karışımların yüzey özelliklerini incelemek için video mikroskop kullanılmıştır. Deri parçacıklarının eklenmesiyle yüzeyde parlaklık oluştuğu gözlemlenmiştir. Hamurların kürleşme özellikleri 160 °C sıcaklıkta reometre cihazı (MDR) ile belirlenmiştir. Reometre ile hamurların vulkanizasyonu sırasında akma davranışı ve reometre parametreleri elde edildi. Bu parametreler; minimum viskosite (M_L), maksimum tork değeri (M_H), ön pişme süresi (t_{s2}), M_L-M_H aralığındaki tork değerinin % 90'ını elde edebilmek için geçen süreyi ifade eden optimum pişme süresi (t_{90}) gibi değerlerdir. Kürleşme süresi 11 ile 21 dakika arasında değişmektedir. 20 phr deri eklenen EPDM kauçuğunun, optimum pişme süresinde önemli bir düşüş gözlemlenmiştir ve dolayısıyla kürleşme oranında artış görülmüştür. M_L and M_H değerleri EPDM kauçuğunun değerleri ile karşılaştırıldığında azalma göstermektedir. 160 °C'de preste pişirilecek olan hamurların miktarının belirlenebilmesi için yoğunluk cihazı ile yoğunlukları ölçüldü. Vulkanizasyon işlemi, reometrede belirlenen pişme süreleri doğrultusunda hidrolik preste 160 °C'de gerçekleşmiştir. Örnekler 2 mm kalınlığında plakalar halinde hazırlandı. Hazırlanan örnekler kesme aletiyle papyon şeklinde kesildi. Vulkanizasyon prosesinden sonra örneklerin kopma ve yırtılma dayanımı, kopmadaki uzama ve %50 sekant modul değerleri gibi mekanik özellikleri çekme testleri ile belirlendi. Sertlikler Shore A tipi sertlik ölçüm cihazıyla belirlendi. EPDM kauçuğuna 0-20 phr deri parçacıkları eklenmesiyle kopma dayanımı, kopmadaki uzama değerleri bir miktar azalırken, modul değerlerinde önemli bir değişiklik yaşanmamıştır. EPDM/CTL karışımlarının çapraz bağ yoğunluğu çekme testinden elde edilen %50 sekant modul değerleri kullanılarak hesaplanmıştır. Sertlik değerleri az oranda artış göstermiştir. Yırtılma direnci 0-20 phr deri eklenmesiyle önemli derecede artış göstermiştir. Bu artış malzemede oluşabilecek herhangi bir çatlamanın büyümesini engelleyecektir.

Isıl ağırlık ölçümü (TGA), karışımdaki maddelerin bozunarak kütle kayıplarının hesabı için kullanılmıştır. İlk kütle kaybı 320-350 °C arasında karışımın yapısında bulunan yağdan kaynaklanmıştır. İkinci kütle kaybı 450-470 °C arasında kauçuğun bozunmasından kaynaklanmıştır. Üçüncü kütle kaybı ise 670-690 °C arasında karbon siyahından kaynaklanmaktadır. 750 °C'den sonra karışımın yapısında inorganik dolgu maddeleri kalmıştır.

Farklı oranlardaki 2 mm kalınlığındaki plakalar 70 °C'de 70 saat boyunca ısıl yaşlandırmaya tabi tutulmuştur. Yaşlandırmadan sonra mekanik özellikler incelenmiştir. Yaşlandırmadan sonra örneğin kopma dayanımı ve kopmadaki uzama değerlerinde önemli bir değişiklik olmamıştır. EPDM kauçuğu ısıya karşı dirençli bir malzemedir. Aynı şekilde EPDM kauçuğuna deri eklenmesiyle de EPDM/CTL örnekleri ısıya direnç göstermiştir. %50 sekant modul değerlerinde önemli bir değişiklik görülmemekle birlikte bir miktar artış görülmüştür. Sertlik değerlerinde de buna paralel olarak yaşlandırma öncesi değerlerle kıyaslandığında bir miktar artış gözlenmiştir. Yaşlandırma sonrası yırtılma direncinde bir miktar azalma görülmüştür. Baskı altında kalıcı deformasyon testi için 160 °C'de 6 mm kalınlığında ve 50 mm çapında plakalar hazırlanmıştır. Hazırlanan örnekler 70 °C'de 70 saat

boyunca metal kalıpları arasında orijinal kalınlığının %25'i kadar sıkıştırılmıştır. Kalıcı deformasyon değerlerinde çok önemli bir değişiklik olmamakla birlikte, bir miktar düşüş gözlenmiştir. CTL parçacıkları eklendikçe, sıkışılabilirlik özelliğinde EPDM kauçuğu ile kıyaslandığında artış gözlemlenmiştir.

1. INTRODUCTION

Rubber compounds are probably the most complex and most widely used class of materials. The ability of raw rubber to be compounded with various chemicals, with other polymers and with fillers like silica, carbon black, clay in fairly high concentrations, enables these compounds to achieve a wide range of properties. Tyres, shoe soles, belts, pulleys and gaskets are all examples of products requiring carefully optimised formulations, where precise amounts of many different components are present (White J., De S. K. and Naskar K.,2009).

The reinforcement of rubber, which results in a pronounced increase of tensile strength, improved tear and abrasion resistance as compared to the neat elastomer, depends to a large extent on the molecular, chemical and rheological characteristics of the elastomer, on the filler properties and on the mixing process and technology. In particular, to cause a significant reinforcement the filler must have high specific surface area that, together with loading, determines the effective contact area between filler and polymer (White J., De S. K. and Naskar K.,2009).

Ethylene propylene diene monomer (EPDM) is a low unsaturated polyolefin developed by DuPont in the 1960s. EPDM has attracted much attention and showed a tremendous growth in market share due to their inherent resistance to heat, aging and oxidation compared to other synthetic rubbers. High mechanical, electrical and dynamic properties as well as low temperature flexibility and excellent resistance to swelling by several chemicals such as brake fluid and glycol. It also has the ability to accept high loading of fillers, reinforcing materials and plasticizers. All these remarkable properties makes it the most suitable rubber for outdoor applications, automotive sealing systems, building profiles, electrical power cable insulation, roofing sheets, belting and sporting good (Ismail H. and Mathialagan M., 2011).

Leather is a natural polymer consisting of collagen fibers crosslinked in a three-dimensional structure; the conventional leather tanning results in improved appearance, physical, chemical and biological properties of leather. (El-Sabbagh S. H. and Mohamed O. A., 2011). Tanning is the key process that renders stability to

the skin matrix against microbial degradation, heat, sweat etc. Chromium (III) has been used widely in tanning for the excellent properties that it renders to the leather along with simplicity of operation (Ramasami T. and Sreeram K. J., 2003). Collagen is the fibrous protein responsible in the formation of skin/hide through various hierarchical organizations and form basis material in leather making. The overall tanning process is classified into four main steps as pre-tanning for the removal of non-collagenous materials, tanning for the stabilization of the collagen matrix, post-tanning to impart functional properties and finishing to give aesthetics. Various chemicals employed in these unit operations have to diffuse through the pores of skin/hide (Sivakumar V., Swaminathan G., Rao G. P., Muralidharan C., Mandal A. B. and Ramasami T., 2010).

In this study, chrome tanned leather pieces were added into EPDM rubber at different compositions using banbury mixer and two roll mill. The effect of different leather loading on the curing, thermal, mechanical and morphological properties of EPDM composites were investigated. For this purpose, previously, curing properties of uncured rubber compounds were obtained using moving die rheometer (MDR). Densities were measured using density measurement device. Differential scanning calorimeter (DSC) was used to determine of glass transition temperature and curing peak enthalpies of uncured composites. The samples were prepared by vulcanizated in hot press at 160 °C measured times.

Thermal gravimetric analysis (TGA) was used to examine the first, second and third mass loss of samples. Mechanical characterization was made using universal testing machine to measure the tensile strength, elongation at break, modulus, tear strength of samples and durometer to measure their hardness. Crosslinking densities of samples were determined according to modulus value. All samples were subjected to thermal aging at 70 °C during 70 hour. The same mechanical properties were applied to the prepared samples to investigate the effects of the aging to the properties.

2.THEORETICAL PART

Elastomers (natural and synthetic rubber) are amorphous polymers to which various ingredients are added, creating what the rubber chemist refers to as a compound. After heating and reaction (vulcanization), these materials become “rubber”. While they are elastic and rubbery, they also dissipate energy because of their viscoelastic nature. Their strength is high, especially under shear and compressive deformations (Hertz, 2012).

The dictionary definition of rubber is, ‘a material that when stretched returns quickly to its ‘approximate original shape’. This definition fits the vulcanized material quite well (Ciesielski, 1999).

2.1 History of Rubber

The first commercial method for vulcanization has been attributed to Charles Goodyear. His process (heating natural rubber with sulfur) was first used in Springfield, Massachusetts, in 1841. Thomas Hancock used essentially the same process about a year later in England. Since those early days, there has been continued progress toward the improvement of the process and in the resulting vulcanized rubber (Mark J. E., Erman B., and Eirich F. R., 2005).

2.2 Types of Rubber

2.2.1 Natural rubber

Natural rubber was the only high polymeric material serving humanity until the advent of polymer technology. Hence the term ‘rubber’ until that point only referred to this natural substance. Since its discovery, the use of rubber has become widespread; when worldwide demand increased, the natural rubber available was inadequate. This made it necessary for scientists to obtain substitutes for natural rubber (Chandrasekaran V. C., 2009).

Natural rubber from Hevea brasiliensis is a natural polymer composed of an association of poly (cis-1,4-isoprene) [poly(2-methyl-1,3-butadiene)] and biological elements, giving it highly specific properties (Höfer R., 2009).

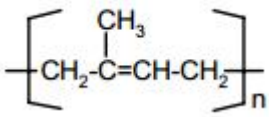

Figure 2.1 : Chemical structure of natural rubber.

Characteristic features of natural rubber make it indispensable to contemporary society. It seems probable that natural rubber will contribute to sustainable development for the foreseeable future.

Currently, the main natural rubber-producing countries are Thailand, Indonesia, Malaysia, India, China, Sri Lanka and Vietnam. As the demand for natural rubber grows, Cambodia, Laos, Bangladesh and some African countries may also become major producers (Kohjiya S. and Ikeda Y., 2014).

2.2.2 Synthetic rubber

Synthetic rubbers (elastomers) are long-chain polymers with special chemical and physical as well as mechanical properties. These materials have;

- Chemical stability,
- High abrasion resistance,
- Strength,
- Good dimensional stability.

Many of these properties are imparted to the original polymer through crosslinking agents and additives. Selected properties of some elastomers are shown in Table 2.1. An important property of elastomeric materials is their ability to be stretched at least twice their original length and to return back to nearly their original length when released (Matar S. and Hatch L. F., 2001).

Table 2.1 : Selected properties of some elastomers (Matar S. and Hatch L. F., 2001).

	Durometer hardness range	Tensile strength at room temp, psi	Elongation at room temp, %	Temp. range of service °C	Weather resistance
Natural rubber	20-100	1000-4000	100-700	-55 - 80	Fair
SBR	40-100	1000-3500	100-700	-55 - 110	Fair
Polybutadiene	30-100	1000-3000	100-700	-60 - 100	Fair
Polyisoprene	20-100	1000-4000	100-750	-55 - 80	Fair
Polychloroprene	20-90	1000-4000	100-700	-55 - 100	Very good
Polyurethane	62-95	1000-8000	100-700	-70 - 120	Excellent
Polyisobutylene	30-100	1000-3000	100-700	-55 - 100	Very good

2.2.2.1 Ethylene propylene diene monomer (EPDM)

EPDM rubber, along with the copolymer of ethylene or propylene (EPM), forms a class of rubbers called ethylene-propylene. However, since EPDM, the terpolymer, is in much greater use than EPM, the former is frequently called ethylene-propylene rubber (Wegman R. F. and Twisk J. V., 2013).

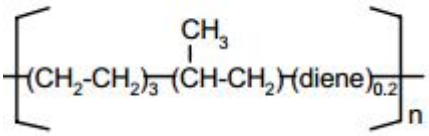

Figure 2.2 : Chemical structure of EPDM.

“Diene” rubbers contain substantial chemical unsaturation in their backbones, causing them to be rather susceptible to attack by oxygen, and especially by ozone. (Hamed, 2012)

EPDM rubbers are amorphous polymers. Like any other non crystallising polymeric materials, the mechanical properties of the unfilled EPDM rubbers are very poor and as a result, addition of reinforcing fillers becomes important for giving strength to this rubber. Usually easy processing, semi reinforcing carbon blacks are used in EPDM compounds. Its low density enables use of high loadings of extender oils and inert and semi reinforcing fillers from the point of view of economic consideration. General curing system for EPDM rubbers will be a thiazole (mercaptobenzothiazole

or dibenzothiazole disulfide) accelerator with a thiuram and/or a dithiocarbamate (Chandrasekaran V. C., 2009).

Properties of EPDM;

- Excellent resistance to atmospheric aging and oxygen.
- Good ozone resistance.
- Very good resistance to water absorption.
- Relatively low cost.
- Very poor resistance to mineral oils and di-ester based lubricants.
- Combined with good mechanical properties.
- Excellent resistance to heat.
- Excellent electrical resistance.
- Resistant to polar solvents like water, acids, alkalies, phosphate esters and many ketones and alcohols (Ciesielski A., 1999).

2.2.2.2 Styrene-butadiene rubber (SBR)

Styrene-butadiene rubber (SBR), a synthetic copolymer composed of styrene and butadiene, is used more often than any of the other synthetics produced today. Many types of SBR rubber are available in oil extended and black masterbatch forms to serve specific applications. SBR has similar resistance to solvents and chemicals as natural rubber, and it can be successfully bonded to a wide range of materials (Massey L. K., 2003).

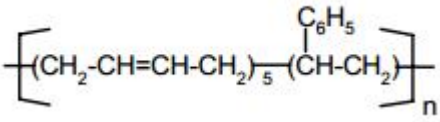

Figure 2.3 : Chemical structure of SBR.

SBR, also known as a non-polar rubber, has good mechanical properties and does not easily break down. Particularly, it has better ozone resistance, weatherability and abrasion resistance than natural rubber (Noriman N. Z., Ismail H. and Rashid A. A., 2009).

2.2.2.3 Polybutadiene (BR)

Polybutadiene is only second to SBR in total synthetic rubber consumption. Nearly 70% of all BR is used for treads and sidewalls of tires. BR has excellent abrasion resistance and low temperature resistance. In fact, only silicone rubber has a lower temperature resistance. However, BR is difficult to process and exhibits poor wet traction properties and is therefore predominantly used in blends with natural rubber and SBR for tires (Stritzke B., 2009).

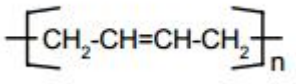

Figure 2.4 : Chemical structure of BR.

The following characteristics are evident:

- Good gas permeability and transparency.
- Low melting point.
- Flexibility.
- Self-adhesiveness (Massey L. K., 2004).

2.2.2.4 Acrylonitrile-butadiene rubber (NBR)

Nitrile rubber (NBR) is a copolymer of acrylonitrile and butadiene and is mainlymade by emulsion polymerization. This rubber is one of the most-used commercial rubbers for manufacturing technical rubber goods. By selecting an appropriate acrylonitrile content, one can tailor the different properties in order to use NBRfor different applications like roll covers, hydraulic hoses, conveyor belting, oil field packers, seals for all kinds of plumbing and appliances.

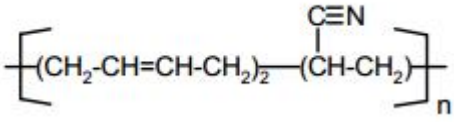

Figure 2.5 : Chemical structure of NBR.

It has excellent temperature resistance properties with a wide short-term and long-term operating temperature range. Like most unsaturated thermoset elastomers, NBR requires formulating with added ingredients, and further processing to make useful

articles. Additional ingredients typically include reinforcement fillers, plasticizers, weather protectants, and vulcanization packages (Heinrich G, 2011).

2.2.2.5 Butyl rubber (IIR)

Butyl rubber is one of the older synthetic rubbers, having been developed in 1937. Because of the saturated nature of a polyolefin elastomer, the commercial polymer is actually a copolymer of isobutylene and isoprene. The isoprene isadded to provide cure sites. In addition, halogenated (bromo or chloro) derivatives are available. The halogenated products improve the mixing and cure compatibility with the more common unsaturated rubbers such as natural or SBR.

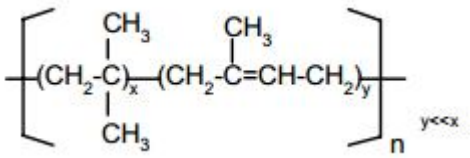

Figure 2.6 : Chemical structure of butyl rubber.

The most important characteristics of butyl rubber are its low permeability to air and its thermal stability. These properties account for its major uses in inner tubes, tire inner liners, and tire curing bladders. Because of the poor compatibility of butyl with other rubbers (with respect to both solubility and cure), the halobutyls are preferred. The brominated p-methylstyrene-containing butyl rubbers are used in a number of grafting reactions for tire applications and adhesives. Other uses for butyl rubber are automotive mechanical parts (due to the high damping characteristics of butyl), mastics, and sealants (Kent J. A., 2012).

2.2.2.6 Neoprene (CR)

Neoprene is the generic name for polymers of chloroprene (2-chloro-1,3-butadiene) (Wegman R. F. and Twisk J. V., 2013). The chains of CR are sufficiently regular in structure to crystallize on stretching. Hence neoprene exhibits high gum tensiles and is used in the pure gum form in many applications.

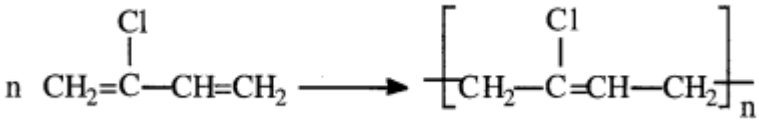

Figure 2.7 : Chemical structure of neoprene (Matar S. and Hatch L. F., 2001)

The vulcanization of neoprene is quite different from the elastomers considered so far. Unlike the others, it is not vulcanized by means of sulfur. Instead, use is made of the fact that the chlorine atoms on the chain can react to some extent with active metal oxides. Hence, zinc oxide or magnesium oxide are used to combine with some of the chlorine and interlink the polymer chains at those sites (Morton M., 1999).

Figure 2.8 : Typical polychloroprene chips.

2.2.2.7 Isoprene rubber (IR)

Natural rubber is a stereoregular polymer composed of isoprene units attached in a cis configuration. This arrangement gives the rubber high resilience and strength. Isoprene can be polymerized using free radical initiators, but a random polymer is obtained. As with butadiene, polymerization of isoprene can produce a mixture of isomers. However, because the isoprene molecule is asymmetrical, the addition can occur in 1,2-, 1,4- and 3,4- positions (Matar S. and Hatch L. F., 2001).

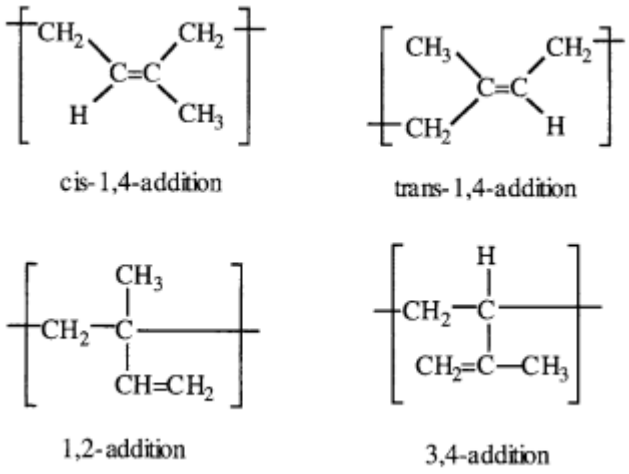

Figure 2.9 : Chemical structure of polyisoprene (Matar S. and Hatch L. F., 2001).

Polyisoprene is a synthetic polymer (elastomer) that can be vulcanized by the addition of sulfur.

cis-Polyisoprene has properties similar to that of natural rubber. It is characterized by high tensile strength and insensitivity to temperature changes, but it has low abrasion resistance. It is attacked by oxygen and hydrocarbons.

trans-Polyisoprene is produced from the leaves and bark of the sapotacea tree. It has different properties from the cis form and cannot be vulcanized. Few commercial uses are based on trans-polyisoprene (Matar S. and Hatch L. F., 2001).

2.2.2.8 Silicone rubber

Silicone rubber is a semiorganic synthetic. Its structure consists of a chain of silicon and oxygen atoms rather than carbon and hydrogen atoms, as inthe case with other types of rubber. The molecular structure of silicone rubber results in a very flexible but weak chain. Silicones are very stable at low and high temperatures. Although fillers may improve properties somewhat, tear and tensile strengths remain relatively low (McKeen L. W., 2012).

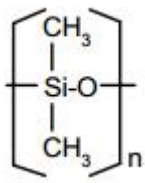

Figure 2.10 : Chemical structure of silicone rubber.

Table 2.2 : Silicones: Key performance attributes and main industrial application (Dodiuk H. and Goodman S. H., 2014).

Key Performance Attributes	Main Applications
Lubricity, substantivity	Personel care, laundry care, textile finishing, lubricants
Surface activity	Defoaming; release coating/additives
Use in ideal temperature range	Rubbers, sealants
Biocompatibility	Medical, surgical
Low electrical conductivity and low dielectric constant	Electrical insulating products
Resistance to oxidation	Seals, cables and heat transfer apps.
Durability and water repellency	Construction, textiles

2.3 Basic Rubber Compounds

For nearly all applications, ingredients are added to a raw elastomer and the resulting mixture is called a compound. The addition of these ingredients affects not only the end-use properties but also the processing behavior of a compound. A generic compound would likely contain at least the materials listed in Table 2.3 (Sommer J. G., 2009).

Table 2.3 : Generic elastomer compound (Sommer J. G., 2009).

Material	Function
Elastomer or blend of elastomer	Provide rubbery behaviour to the compound
Fillers	Modify modulus and processing properties
Pasticizers	Reduce viscosity and alter properties
Protective agents	Protect compound from oxygen and ozone
Vulcanization additives	Crosslink elastomer chains

2.3.1 Raw Gum Elastomer

The rubber recipe (or formulation) is the heart of rubber technology. This is the key ingredient (the one which is actually cross-linked) on which depend many of the properties of the final product. It is therefore always at the top of the formulation list and is expressed as 100 parts by weight of the total recipe. It is accepted convention in the rubber industry to base all part levels as "parts per hundred rubber" or "phr." This means that the total parts of one, two,three, or more different rubbers called for in a specific recipe must be defined as 100. Thus, all the other nonrubber ingredients

are ratioed against this "100 parts" (that represents all the rubber hydrocarbon). (Hewitt N., 2007)

The compound formulation in Table 2.4 is a typical one in the rubber industry for most unsaturated (sulfur cross-linked) elastomers. The following sections consider ingredients individually (Ciesielski A., 1999).

Table 2.4 : The basic compound formula (Ciesielski A., 1999).

		Specific Formulation	
Material	phr	For Example	phr
Raw gum elastomer	100	SMR 20	100
Sulfur	from 0 to 4	Sulfur	0.35
Zinc oxide	5	Zinc oxide	5
Stearic acid	2	Stearic acid	2
Accelerators	from 0.5 to 3	MBS TMTD	1.4 0.4
Antioxidant	from 1 to 3	HPPD	2
Filler	from 0 to 150	N330 Black	45
Plasticizer	from 0 to 150	Aromatic petroleum oil	4
Miscellaneours		None	
		TOTAL	160.15

2.3.2 Fillers

Rubbers (or elastomers) are in general not used in their purest form, but are reinforced with fillers as unfilled rubbers are generally not very strong. The addition of fillers fundamentally changes the properties of rubber. The modulus of unfilled rubbers rises with increasing temperature, as predicted by the kinetic theory of rubber elasticity. The addition of fillers significantly changes the temperature coefficient of the modulus, it can even alter the sign of the coefficient, resulting in a decrease of the modulus with increasing temperature. Another effect of blending rubbers with fillers is the transition to non-linear behaviour. The use of reinforcing fillers gives the material unique properties:a combination of high elasticity and high strength (White J., De S. K. and Naskar K., 2009).

In order for a filler to cause significant reinforcement, it must possess high specific surface area, i.e., the particles must be small, less than about 1 μm in size. Small particles have large surface areas to interact with the rubber and close particle-to-

particle spacing in the compound. Two types of fillers that are most effective for reinforcing rubber are carbon black and silica (Hertz D. L. and Gent, N. A**.,** 2012).

2.3.2.1 Carbon black (CB)

Carbon black is the most important commercial reinforcing filler and is extensively used when high strength is essential. CB constitutes approximately 30% of the filler used in the rubber industry. The addition of carbon black can affect virtually all phases of a rubber factory's operation as well as the performance characteristicsof the end product due to its unique properties, which can produce strong interactions with any rubber, from tire components to industrial rubber products (Nabil H., Ismail H. And Azura A. R., 2012).

The physical properties imparted to a given rubber compound by carbon black are dominated by three factors: 1) the loading of the carbon black, 2) the specific surface area of the carbon black, and 3) the structure of the carbon black. Table 2.5 shows a generalization of how these factors influence the rubber properties.

Table 2.5 : Effect of carbon black on rubber properties (Rodgers B., 2004).

	Effect of increase in carbon black properties		
Rubber property	Surface area	Structure	Loading
Uncured properties			
Mixing temperature	Increases	Increases	Increases
Die swell	Decreases	Decreases	Decreases
Mooney viscosity	Increases	Increases	Increases
Dispersion	Decreases	Increases	Decreases
Loading capacity	Decreases	Decreases	-
Cured properties			
300% modulus	Insignificant	Increases	Increases
Tensile strength	Increases	Insignificant	Increases[a]
Elongation	Insignificant	Decreases	Decreases
Hardness	Increases	Increases	Increases
Tear resistance	Increases	Decreases	Increases[a]
Hysteresis	Increases	Insignificant	Increases
Abrasion resistance	Increases	Insignificant	Increases[a]
Low strain dynamic modulus	Increases	Insignificant	Increases
High strain dynamic modulus	Insignificant	Increases	Increases

[a] Increases to an optimum, then decreases.

2.3.2.2 Silica

Although the use of carbon black results in outstanding high reinforcement, non-black fillers such as clays, carbonates, silicates, and precipitated silica are also

needed that differ not only in their chemical structure but also in their particle size and shape. Compared to carbon black these fillers show advantages in cut and flex resistance and heat build up, they are nonconducting, andthey are required for colored products, but the reinforcement they provide with regard to modulus and abrasion resistance, is limited (Rodgers B., 2004).

2.3.3 Activators

2.3.3.1 Zinc Oxide (ZnO)

Zinc oxide (ZnO) is an important inorganic pigment for the rubber industry, and over the past 100 years, rubber industry has utilized an increasing number of physical and chemical properties of ZnO. ZnO is an important inorganic pigment for the rubber industry, and over the past 100 years, rubber industry has utilized an increasing number of physical and chemical properties of ZnO.

ZnO finds wide application because of its photochemical properties and chemical reactivity. ZnO has proved to be the most cost effective inorganic pigment to activate the rate of sulfur cure with the accelerators. ZnO is also widely used as a UV stabilizer and as an additive having biocidal activity. Remaining in the invisible form in the finished product, zinc has long been used as an essential compounding ingredient in rubber. It was one of the first pigments extensively used in the rubber products manufacturing (Sahoo S., Maiti M., Ganguly A., George J. J. and Bhowmick A. K., 2007).

2.3.3.2 Stearic acid

This is the other principle activator that is used in the vast majority of rubber compounds with zinc oxide to activate the cure. It is generally known that stearic acid reacts with the zinc oxide in the rubber compound to produce a salt that reacts with the rubber accelerator to initiate an effective vulcanization. What the rubber industry calls "rubber grade stearic acid" is not pure stearic acid. The grade of "stearic acid" selected as a rubber compounding ingredient is usually a mixture of stearic acid, palmitic acid, and oleic acid as derived from hydrolysis of triglycerides from tallow or fats from other animal or vegetable sources (Dick J. S., 2003).

Organo-amines have been used to render silicate surfaces hydrophobic, bonding probably through strong coordinate bonds. These relatively labile coatings will help

improve dispersion in the initial stages of a compounding operation, before they desorb. They also give a protective coating to the filler, minimising any polymer degradation that may occur before stabilisers, antioxidants, etc., are fully dispersed (Rothon R. N., 2003).

2.3.4 Antioxidant

Antioxidants are very important additives whose role it is to maintain the chemical and physical properties of different materials such as plastics, elastomers, processed food, lubricants, etc., during transportation, storage, processing, and serving conditions. Antioxidants, also called antidegradants in the rubber industry, protect elastomers against aerobic aging (oxygen) and ozone attack. They are prime importance and play a vital role in the rubber products maintaining their properties at service conditions. Although conventional antioxidants provide protection against the deleterious effects of energetic free radicals, they suffer from some serious drawbacks such as poor thermal stability, high volatility, poor processability, etc., owing to their molecular size (Cirilo G. and Iemma F., 2012).

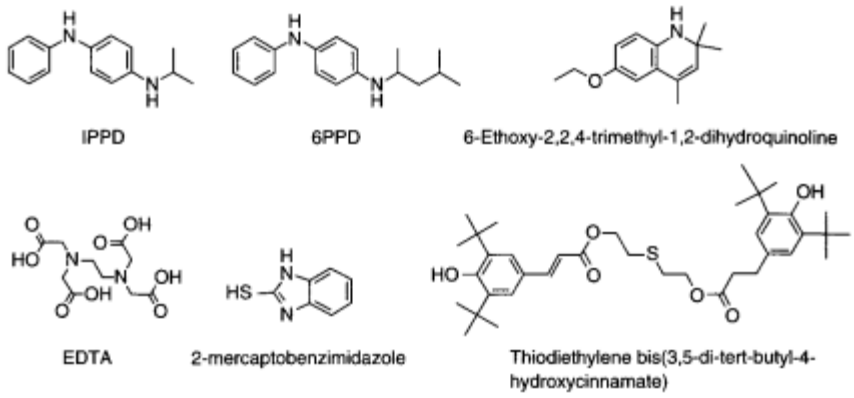

Figure 2.11 : Elastomers antioxidants (Cirilo G. and Iemma F., 2012).

Techniques for providing increased protection against oxidation under severe temperature and solvent extraction conditions include the use of polymer-bound antioxidants. Chemical attachment of the antioxidant molecule to the polymer backbone eliminates volatility and extraction by making the antioxidant essentially infinite in molecular weight after curing. Two general methods of accomplishing this attachment have been used:

1. functionalized macromolecules react with antioxidant molecules to provide the bound antioxidant, and

2. antioxidant molecules containing polymerizable functional groups may be copolymerized with conventional monomers during polymer production (Baker C. S. L. and Fulton W. S., 2012).

2.3.4 Vulcanization Process

Unvulcanized rubber is generally not very strong, does not maintain its shape after a large deformation, and can be very sticky. In short, unvulcanized rubber can have about the same consistency as chewing gum.

Vulcanization is a process generally applied to rubbery or elastomeric materials. These materials forcibly retract to their approximately original shape after a rather large mechanically imposed deformation. Vulcanization can be defined as a process which increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus vulcanization increases elasticity while it decreases plasticity. It is generally accomplished by the formation of a crosslinked molecular network (Figure 2.12) (Mark J. E., Erman B., and Eirich F. R.,2005).

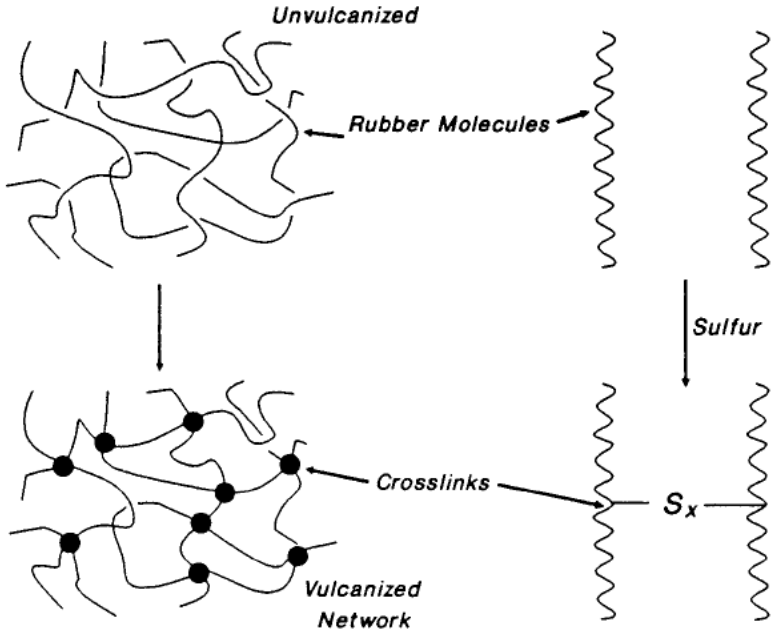

Figure 2.12 : Network formation

Vulcanization, thus, is a process of chemically producing network junctures by the insertion of crosslinks between polymer chains. A crosslink maybe a group of sulfur atoms in a short chain, a single sulfur atom, a carbon to carbon bond, a polyvalent

organic radical, an ionic cluster, or a polyvalent metal ion. The process is usually carried out by heating the rubber, mixed with vulcanizing agents, in a mold under pressure (Mark J. E., Erman B., and Eirich F. R., 2005).

Properties of rubber improved by vulcanization:

- Tensile strength;
- Elasticity;
- Hardness;
- Tear strength;
- Abrasion resistance;
- Resistance to solvents.

2.3.5.1 Sulfur vulcanization

Vulcanization of rubber with sulfur is a process of improvement of the rubber elasticity and strength by heating it in the presence of sulfur, which results in three-dimensional cross-linking of the chain rubber molecules (polyisoprene) bonded to each other by sulfur atoms.

Sulfur is the universal vulcanising agent for natural rubber and also for synthetic rubbers, which contain olefinic unsaturation in the polymer chain. The crosslinks formed during sulfur vulcanisation of olefinically unsaturated rubber are of three types: monosulfidic, disulfidic and polysulfidic. The relative properties of above crosslinks have an implication in the mechanical and ageing behaviour of vulcanisates (Joseph R., 2013).

Vulcanization by sulfur without accelerator;

The use of accelerators in concentrations as low as 0.5 phr has since reduced the time to as short as 1 to 3 minutes. As a result, elastomer vulcanization by sulfur without accelerator is no longer of much commercial significance. Many slow reactions occur over the long period of vulcanization.

Accelerated-sulfur vulcanization;

Accelerated-sulfur vulcanization is the most widely used method. For many applications, it is the only rapid crosslinking technique that can, in apractical manner,

give the delayed action required for processing, shaping, and forming before the formation of the intractable vulcanized network. Frequently, mixtures of accelerators are used. Typically, a benzothiazole type is used with smaller amounts of a dithiocarbamate (thiuram) or an amine type. An effect of using a mixture of two different types of accelerator can be that each activates the other and better-than-expected crosslinking rates can be obtained. Mixing accelerators of the same type gives intermediate or average results (Mark J. E., Erman B., and Eirich F. R.,2005).

2.3.5.2 Peroxide vulcanization

Peroxides are another type of curing agent for elastomers. Unlike sulfur curing, double bonds are not required for peroxide vulcanization, and thus, they may be used to crosslink saturated rubbers. Peroxide curing occurs by a free radical mechanism and leads to carbon-carbon crosslinks, which are quite stable and result in good aging and compression set resistance (Bauman J. T., 2008).

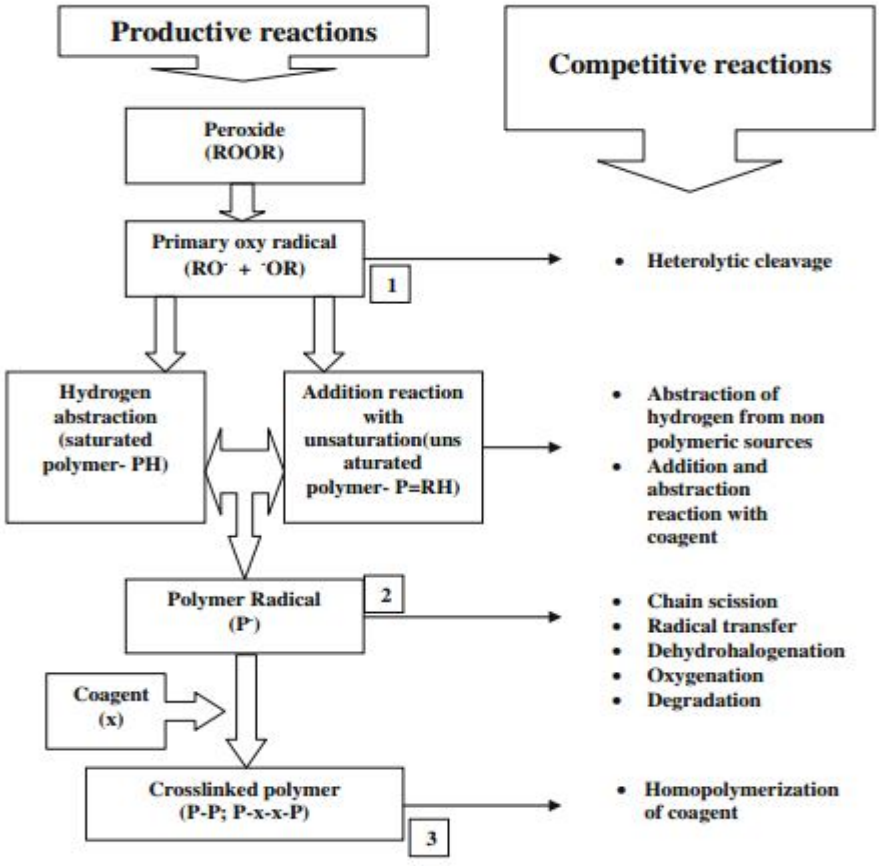

Figure 2.13 : Various productive and competitive reactions involved in coagent assisted peroxide crosslinking system (Visakh P. M., Thomas S., Chandra A. K. and Mathew A. P., 2013).

The major advantages of using peroxide crosslinking system are:

- Improved high temperature resistance
- Reduced compression set
- Ability to crosslink saturated as well as unsaturated rubber
- Rapid vulcanization without reversion
- Formation of C–C bond, which is similar to the bond strength to every other bond in polymer backbone (Visakh P. M., Thomas S., Chandra A. K. and Mathew A. P., 2013).

2.3.5.3 Accelerator

Accelerators play a vital role for vulcanization of rubber. The physical and chemical properties of the vulcanizates depend on the type of the accelerators used and also on the condition of vulcanization. Frequently, the use of two or more accelerators simultaneously, instead of a single one, are found to be more advantageous for technological applications, as these mixed systems generally show higher vulcanization activity (synergism) than the individual accelerators separately. Mixed accelerator systems have, therefore, gathered much attention both from scientific and technical points of view. It is suggested that in a binary accelerator system, the interaction between the accelerators produce reactive compounds, which decompose into free radicals or ions, capable of initiating a reaction between sulfur, rubber and crosslinking process of the latter. Significant contribution with respect to synergistic activity of the binary systems of accelerators during vulcanization of natural rubber (Alam N., Mandal S. K., Roy K. and Debnath S. C.,2013).

2.4 Rubber Equipments and Its Use

Today there is a wide variety of rubber polymers, each with its own set of characteristic attributes, and each offered with modifications designed to enhance one or more of those attributes. In most cases, nevertheless, the elastomer by itself lacks one or more property necessary to produce a saleable product. A number of materials must be added to make it commercially useful. Compounding is the means by which elastomer and additives arecombined to ensure efficient manufacture of the best possible product. Thedesign of a compound formula is the basic function of rubber technology.

The compounding of rubber products starts with the choice of elastomer, filler (reinforcing or extending), crosslinking chemicals, and various additives which, when mixed together, will provide a compound with the desired properties and performance. Mixing is followed by forming operations such as milling, extrusion, and calendering (Cuillo, 1999).

2.4.1 Banbury mixer

The two most commonly employed pieces of equipment for blending rubber and additives are rubber mills and a special type of mechanical mixer known as the Banbury mixer. Figure 2.14 shows the typical Banbury mixers. Each consists of a completely enclosed mixing chamber in which two spiral-shaped rotors, revolving in opposite directions and at different speeds, operate to keep the stock in constant circulation. Most banbury mixers have two wing rotors, but four-wing designs have been developed for faster mixing (Moore A. L., 2006). A ridge between the two cylindrical chamber sections forces intermixing, and the close tolerances of the rotors with the chamber walls results in a shearing action. A floating weight in the feed neck confines the batch within the sphere of mixing. This combination of forces produces an ideally homogeneous batch (Cheremisinoff N. P., 2000).

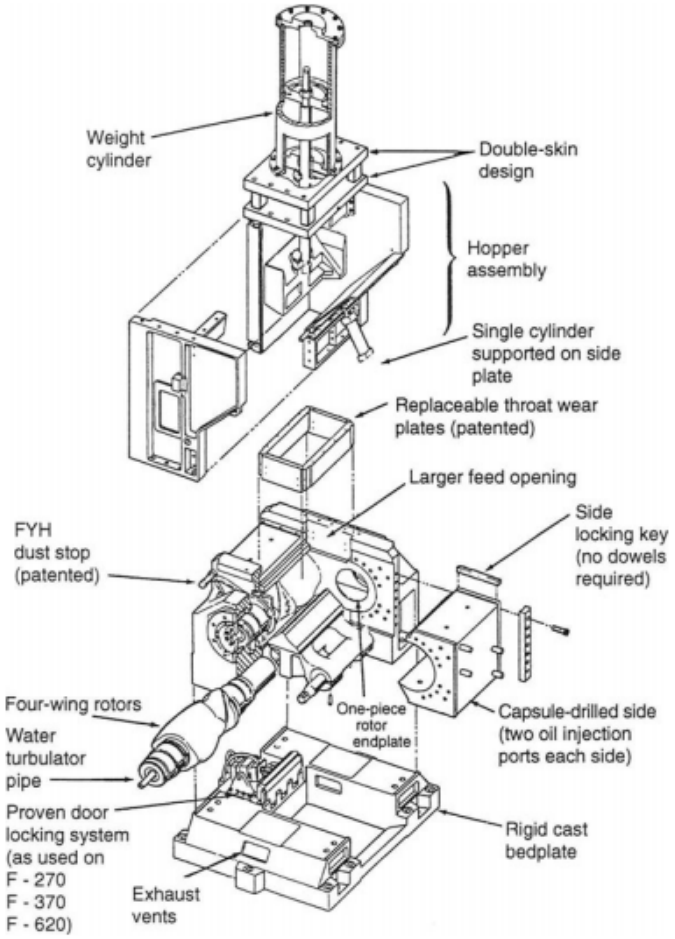

Figure 2.14 : Basic banbury mixer (Melotto M. A., 1997).

2.4.2 Open Mill

Roll mills are used widely in rubber processing. In the mixing process the material to be mixed is drawn into the roll nip. This requires sufficient static friction between the raw rubber and the surface of the two rolls, which rotate with friction. Because of this friction, different forces act on the compound being drawn through and continuously shift the particles toward one another. Compacting then occurs in the roll nip. The different rates at which the materialis drawn through also make the rubber head on the roll nip turn, and thus contribute to homogenization of the compound. The compound is finally homogenized by manual cutting and reintroduction of the sheet formed into the roll nip. The excellent mixing action of the mill is related to the fact that very intensive cooling is possible due to the large surface area; thus, high shearing forces can always be introduced (Langenthal W. V. and Schnetger J, 2002).

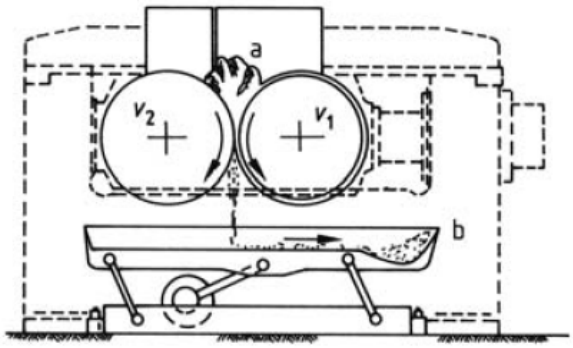

Figure 2.15 : Construction of rubber mill. a) Rubber compound b) Vibrating through(Langenthal W. V. and Schnetger J, 2002)

2.4.3 Molding

Compression molding is among the oldest materials processing techniques. For rubbers, it was one of the first industrial methods, with equipment dating back 100 years. The basic process consists of heating a uncured rubber, under severe pressure, within a closed mold cavity until the compound cures through a chemical reaction of crosslinking polymeric chains (Tatara R. A., 2011).

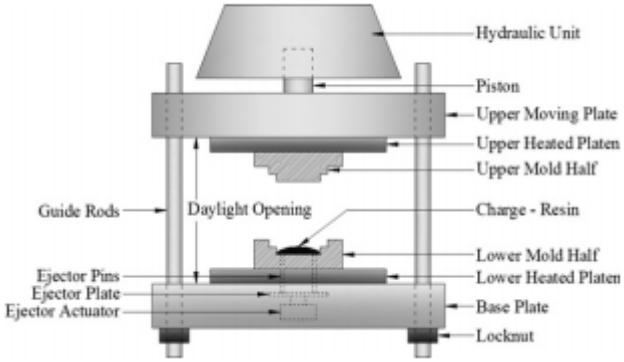

Figure 2.16 : Schematic view of a typical compression press.

2.4.4 Extruder

In rubber processing, extruder is mainly used for shaping the rubber compound into the desired profile before it is finally processed. There are two type of extruder—ram extruder and screw extruder. Ram extruder has high operating cost and lower output. Now, the screw extruder is used mainly for the production of tubing, channel, tire treads and for the insulation of the wire and cables (Visakh P. M., Thomas S., Chandra A. K. and Mathew A. P., 2013).

The extruder consists of a feed hopper, cylindrical barrel, rotating screw, head attachment and a die. The screw is driven by the an electric motor through appropriate reduction gear system. The compound to be shaped is fed into the machine through the feed hopper. The barrel is usually made of hardened steel and is jacketed for the circulation of steam or cold water. Heating of the barrel is necessary in the early stages, when it is started temperature is developed inside in this stage. The head attachment of the extruder varies in shape according to the purpose for which it is used. The die of the extruder shape the compound into the desired profile. For better shape and finish of the extrudate, the design of the dies is very important (Visakh P. M., Thomas S., Chandra A. K. and Mathew A. P., 2013).

2.4.5 Calendering

Calendering is a processing operation that primarily produces rubber sheets of a controlled thickness and it is also used to coat textiles or other materials. The number of rolls on a calender and their geometric arrangement primarily defines the type of calender. Three-roll calender scommonly have the axes of their rolls arranged either vertically or offset; four-roll calender shave the axes of their rolls offset. Three-roll calenders are more commonly used for non-tire compounds; four-roll calenders for tire compounds (Sommer J. G., 2009).

2.5 Leather

Leather is a natural polymer consisting of collagen fibers crosslinked in a three-dimensional structure; the conventional leather tanning results in improved appearance, physical, chemical, and biological properties of leather. At the same time, this industry is highly polluting as it produces large amounts of organic and chemical pollutants. Wastes generated by the leather processing industries pose a major challenge to the environment, according to conservative estimates, about 600,000 tons per year of solid waste are generated worldwide by leather industry, and 40–50% of the hides are lost to shavings and trimmings (El-Sabbagh S. H. and Mohamed O. A.,2011).

The physical properties of chrome tanned leather is shown in the Table 2.6.

Table 2.6 : Physical properties of leather (Bailey D. G., 2011).

Property	Value
Tensile strength, MPa	15.2-37.4
Elongation at break, %	29.5-73.0
Tear strength, N/cm	226-961
Wet shrinkage temperature, °C	96-120
Density, g/cm^3	1.4-1.6

2.5.1 Chemical composition of leather

Fresh cattlehides, like most biological materials, contain 65–70% water, 30–35% dry substance, 9% lipids and <1% ash. The dry substance is largely made up of the fibrous proteins collagen, keratin, elastin, and reticulin.

Collagen, the principal protein of the hide, is the material that is made into leather. The reactivity of the collagen toward tanning agents and the dyeability, as well as the strength, flexibility, and durability of the collagen when tanned, are all important to making leather a material of choice for utility and fashion (Thorstensen T. C, 2000).

Keratin is the sole protein component of hair and the second most common protein in the hide. Depending on the age of the animal and season of the year, keratin may constitute 6–10% of the total protein. One of the first steps in the manufacture of most leather is removal of hair (keratin) from the hide (Bailey D. G., 2011).

2.5.2 Process preparing hides and skins for tanning

Beamhouse operations are the operations carried out to mainly prepare the raw skins and hides for tanning through cleaning the undesired inter-fibrillary material and conditioning. The beamhouse operations are common in all tanning operations irrespective of the type of the subsequent tanning process.

Typically applied beamhouse operations are, soaking, unhairing, liming, deliming, bating and pickling (Orhon D., Babuna F. G. and Karahan O., 2009).

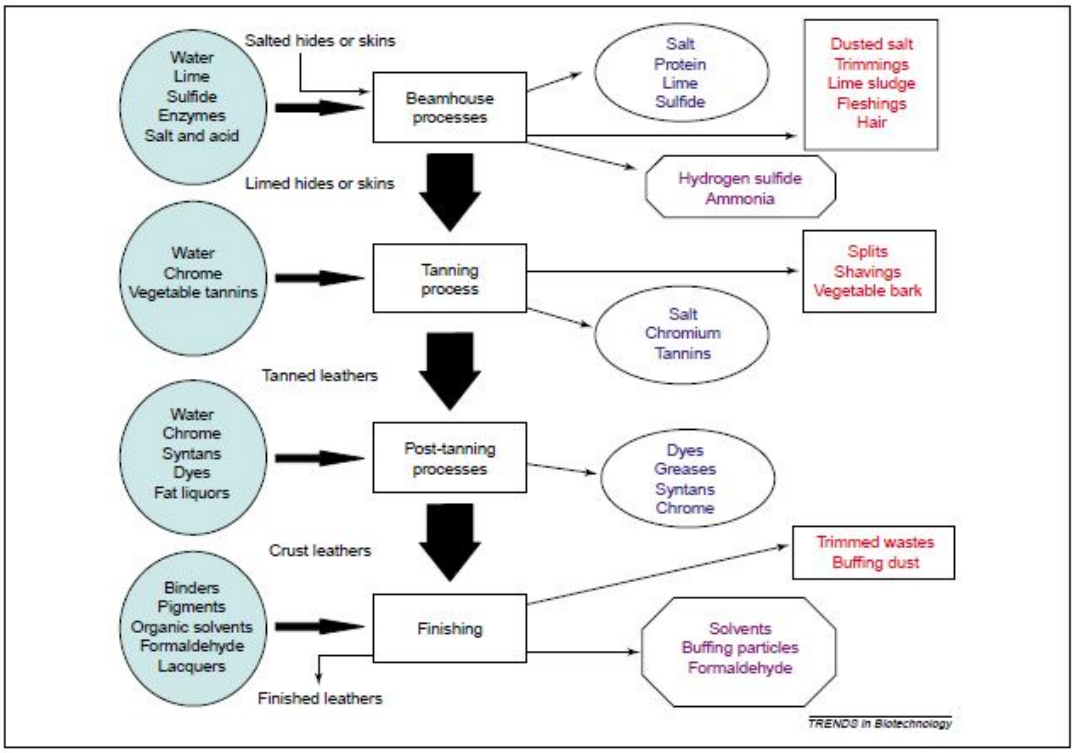

Figure 2.17 : Inflow–outflow diagram for leather processing (Thanikaivelan P., Rao J.R., Nair B. U. and Ramasami T., 2004).

Soaking; the targets of soaking are manifold: Removal of dirt, dung, blood, and salts, mainly NaCl, in the case of hides preserved by salting. The soaking process takes place in drums or very often in mixers (Reich G., 2012).

Unhairing; can be done either by a hair save or a hair pulp system. The hair pulp system is preferred by most tanners for its speed and labor efficiency. In the hair pulp system the hides are treated with sodium sulfide (sulfhydrate) and lime (calcium hydroxide). The hair is quickly destroyed by the strong alkaline reducing conditions. The drum or hide processor is run at slow speeds intermittently during the unhairing process. The continued action of the lime solution on the hides brings the pH to 12–13. At this pH the hides swell to about twice the original thickness. This swelling has a beneficial opening of the fibers to permit better tannage.

Deliming; the limed hides have a pH around 12. Because chrome tanning is done at pH 2–4, the lime must be removed for pH adjustment. In addition, the undesirable materials in the hide, ie, both natural and the degradation products from the unhairing, must be removed. For deliming, ammonium salts and acids are used (Thorstensen T. C, 2000).

Bating; is a generic term that refers to the use of enzymes in an early stage of leather making. Its purpose is to break down specific skin components: usually the non-structural proteins are the target (Covington T., 2009).

Pickling; bated hides or skins are at a near neutral pH and thus are immediately processed, because under the seconditions the protein is subject to bacterial degradation. Pickling is the term used for acidification of the hides. For chrome tanning, the desired pH is about 2.0, thus the hides are placed in a solution of salt and acid (Thorstensen T. C, 2000).

2.5.3 Chrome Tanning Process

Chrome tanning is the most widely used tanning system worldwide (Thorstensen T. C, 2000). The reasons for the popularity of the process are clear, when the features of the process are compared with other tanning process:

- The process time for the chrome tanning reaction itself is typically less than 24 hours, the vegetable tanning reaction takes several weeks, even in a modern process.
- Chrome tanning confers high hydrothermal stability; a shrinkage temperature of 110 °C is easily attainable, this opens up new applications.
- Chrome tanning alters the structure of the collagen in only a small way: the usual chrome content of fully tanned leather is 4% Cr_2O_3 hence the handle and physical properties are inevitably modified, restricting applications of the leather.
- Chrome tanning makes collagen more hydrophobic, so the tannage allows water resistance to be built into the leather.
- Chrome tanned leather is lightfast. Hence, dyed chrome tanned leather will retain its colour better (Covington T., 2009).

Chrome tanning is done in a drum similar to that used for deliming. The salt solution from the pickle is present and the solution is at about pH 2.0. The chrome-tanning material is usually a basic chromium (III) salt.

The general formula for the most common commercial chrome-tanning product is $2Cr(OH)SO_4 \cdot Na_2SO_4$. After the addition of the chrome-tanning salts, the pH of the

solution rises to about 2.5. At this pH the chromium salt is taken up by the hide and the tannage begins.

Control of chromium penetration, essential to permit tannage of the center of the hide, is accomplished by pH adjustment. At a pH ≥ 3.0 the reactivity of the hide to the chromium complex is greatly increased.

The chemistry of chrome tanning involves competing reactions that must be controlled for satisfactory results.

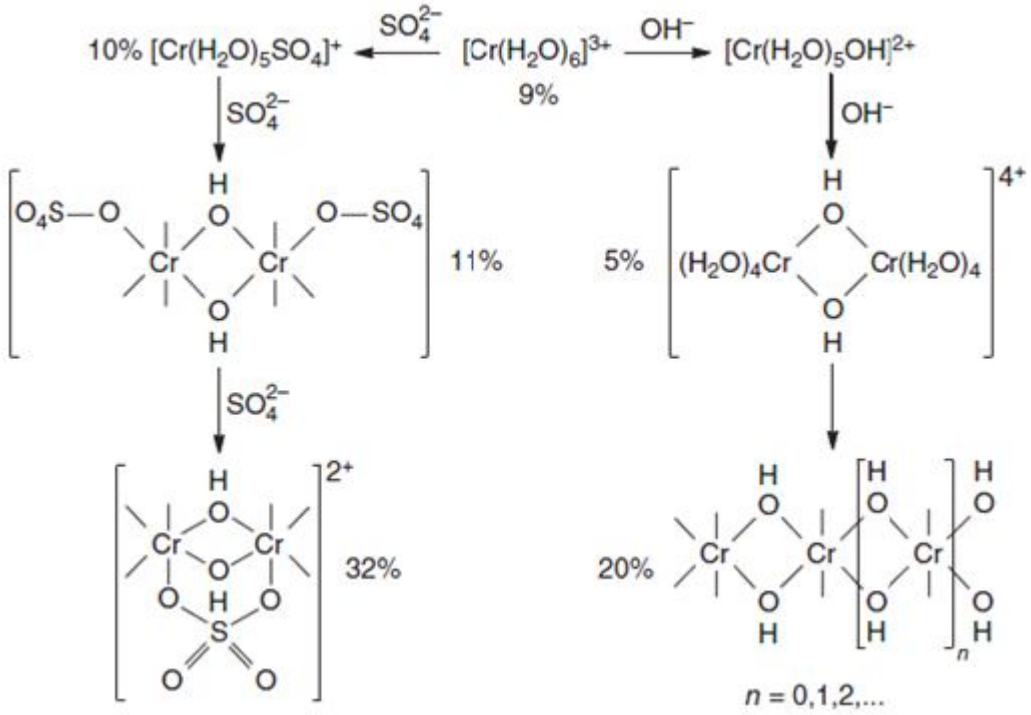

Figure 2.18 : Structures of basic chromium salts (Bailey D. G., 2011).

In summary, chrome tanning is faster, better in all sorts of ways and offers more versatility to the tanner, with regard to the leather that can be made from wet blue, the name given to leather after the chrome tanning reaction is complete (Covington T., 2009).

2.5.4 Vegetable Tanning

Vegetable tannings are water-soluble materials extracted from different parts of certain plants, including the wood, bark, leaves, fruits, pods, and roots. Vegetable tanning produces a fullness and resilience characteristic of only this type of tannage. It has excellent molding characteristics allowing, for example, in sole leather, adaptation to the shape of the foot. Vegetable-tanned leathers have good strength and

dimensional stability. In general, the hide is prepared for vegetable tannage in the same way as for chrome tannage except of reaction takes several weeks (Bailey D. G., 2011).

2.6 Literature Review

Ravichandran et al. have studied scrap rubber recycling in natural rubber using untreated and neutralized fibrous particles of leather shavings (material just tanned with no retanning, fatliquoring, dyeing, or finishing applied) as processing aid. The untreated material being acidic in nature, reduces the vulcanization characteristics and mechanical properties of the compound, but improves the incorporation of higher amount of scrap rubber. To overcome the acidic nature, 1% solution of urea, aqueous ammonia, and sodium bicarbonate were used separately as neutralizing agents. Results indicate that neutralized leather wastes can assist the addition of large quantities of scrap rubber into a virgin rubber matrix without affecting the vulcanization characteristics seriously. Mechanical properties of natural rubber-scrap vulcanizates containing neutralized leather particles are better when compared with the vulcanizates containing untreated leather particles. The natural rubber-scrap compositions containing treated leather could be processed safely in the temperature range of 413-423 K without much reversion in the matrix (Ferreira M. J., Freitas F and Almedia M. F., 2010).

It is possible to use leather waste particles as a filler of polymer. Andreopoulos et al. have incorporated leather wastes into PVC with dioctyl phthalate as plasticizer. The addition of the leather wastes caused that density and hardness of the composites increased, whereas their tensile properties were considerably deteriorated with the incorporation of leather. Leather dust with silica was used as a filler of PVC (El-Sabbagh S. H. and Mohamed O. A., 2011).

Chang et al. have modified the sodium montmorillonite by using octadecyl ammonium ions and incorporated the modified nanoclay into EPDM. They have observed the tremendous improvement in tensile and tear strength (Heinrich G., (2011).

Chronska et al. have investigated the addition of the buffing dust to rubber mixes. They concluded that the mechanical properties are improved, and resistance to

thermal aging as well as electric conductivity and crosslink density of vulcanizates are increased (El-Sabbagh S. H. and Mohamed O. A., 2011).

For decades, layered silicate has attracted considerable attention and been widely used in rubber and plastics industries. More recently, many researches have been carried out on preparation and improvisation of rubber/clay nanocomposites. EPDM/clay hybrid with montmorillonite prepared by Usuki et al., shows an improvements on tensile strength and storage modulus and the permeability decreased 30% compared to unfilled EPDM (Ismail H. and Mathialagan M., 2011).

Polyphenylsilsesquioxane (PPSQ) microspheres with ladder structure synthesized in the laboratory have been incorporated into ethylene propylene diene monomer (EPDM) composite in order to study the effect of PPSQ on the ablative and flame-retardation properties of EPDM composites by Jiany et al. The results showed that PPSQ microspheres serve as an effective ablative additive and flame retardant for EPDM composites. Thus, PPSQ greatly improved the ablative properties of EPDM composites, with a 4.8 wt% loading leading to a remarkable reduction in the linear ablation rate of EPDM by about 50%. Moreover, this loading of PPSQ improved the flame retardancy and smoke suppression, and significantly reduced the PHRR of EPDM composite from 504 kW/m^2 to 278 kW/m^2. Moderate tensile strength could be obtained and the breaking elongation was improved for the EPDM/PPSQ composites. TGA results showed that PPSQ had little influence on the thermal decomposition of EPDM. SEM, CONE, and TG-FTIR tests showed that the char structure of EPDM composites was the primary factor through which PPSQ affected the ablative and flame-retardation properties of EPDM. The chars formed during the ablation of EPDM composites containing PPSQ had better structural stability and thermal stability, owing to the fact that they were denser, remained intact, and had an ordered arrangement of holes (Jiang Y., Zhang X., He J., Yu L. and Yang R., 2011).

Mazinani et al. have investigated the effect of graphene oxide on cure behavior of ethylene propylene diene rubber (EPDM) nanocomposite is studied. In this regard, the cure kinetics of nanocomposite is studied employing different empirical methods. The required activation energy of nth-order cure process shows about 160 kj/mol increments upon 5 phr graphene oxide loading compared to 1 phr graphene oxide loading. However the required activation energy is significantly reduced followed by incorporation of graphene oxide in nanocomposites compared to neat EPDM sample.

As the results show, grapheneoxide interestingly affect the structure of zinc oxide during the vulcanization process. The behavior could be probably related to high tendency of zinc oxide to react with oxidized surface of graphene oxide (Allahbakhsh A., Mazinani S., Kalaee M. R. and Sharif F., 2013).

3. EXPERIMENTAL

3.1 Materials

3.1.1 Ethylene propylene diene monomer (EPDM)

EPDM, DUTRAL TER 4437 with propylene content 32 %, ENB of 4.5 %, ML (1+4) 125 ° C of 57 MU and ash content of 0.3 max. % was obtained from Polimeri Europa Company, Inc. It was used as rubber matrix.

3.1.2 Chrome tanned leather (CTL)

Chrome tanned leather shavings were obtained from Atik Leather Company Co.Ltd, Tuzla Organized Leather Industry and then cut into smaller pieces. It has no Cr^{+6} and 22000-23000 ppm Cr^{+3}. Its pH is 4 and moisture content is 36.76 %.

3.1.3 Carbon black (CB)

Carbon black, FEF N-550 with CTAB ADS of 40 m^2/g, density of 0.35 g/cm^3 and pH=7 was obtained from Tüpraş Petroleum Refineries Corporation, Turkey. It was used as filler.

3.1.4 Paraffinic oil

Paraffinic oil 460 was obtained from Petrol Ofisi Inc, Turkey. Its density is 0.908 gr/ml and flashing point is above from 285 °C.

3.1.5 Zinc oxide (ZnO)

Zinc oxide with min 35.50% zinc was obtained from Hepşen Chemical Company Co.Ltd, Turkey. It was used for activator.

3.1.6 Stearic acid

Stearic acid was obtained from Kimpaz Chemical Company Co.Ltd, Turkey. It was used for activator.

3.1.7 Sulfur

Sulfur, Rhenogran S-80 with 80% sulfur, 20% elastomer binder and dispersing agents was obtained from Lanxess Co.Ltd, Turkey. Its density is 1.64 g/cm^3 approximately. It was used as curing agent.

3.1.8 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ)

Vulcanox HS/LG with 1.04 g/cm^3 density, 90 °C softening point and below 0.3 % ash content was obtained from Lanxess Company Co.Ltd, Turkey. It was used as antioxidant.

3.1.9 N-isopropyl-N'-phenyl-p-phenylene-diamine (IPPD)

Vulcanox 4010 NA/LG with 1.04 g/cm^3 density, 76 °C melting point and 0.1 % ash content was obtained from Lanxess Company Co.Ltd, Turkey. It was used as antioxidant.

3.1.10 Tetramethyl thiuram disulfid (TMTD)

TMTD was obtained from DeltagranCompany Co.Ltd and used as accelerator.

3.1.11 2-Mercaptobenzothiazole (MBT)

MBT was obtained from Deltagran Company Co.Ltd. and used as accelerator.

3.2 Equipments

3.2.1 Equipments used for compounding

3.2.1.1 Moisture analyser

Moisture of CTL were measured using Ohaus MB 45 moisture analyser. Device has halogen lamp and precision is 0.001%.

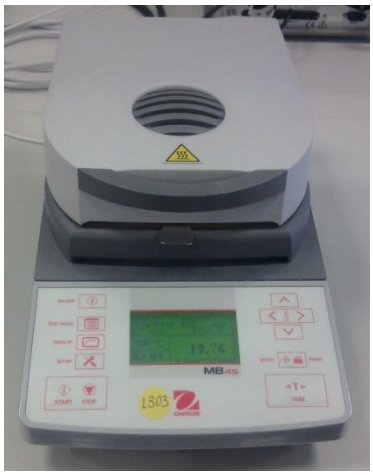

Figure 3.1 : Moisture analyser.

3.2.1.2 Sieve analyser

Sieve analyser was used to determined of particle size distribution of CTL shavings using in Figure 3.2 below device. Different mesh sizes of pans were added up and it was sifted at 50 Amplitude during 10 minutes. Then weights were measured in the pans and seperation was completed.

Figure 3.2 : Sieve analyser device.

3.2.1.3 Banbury mixer

The compounding of EPDM, CTL and other ingredients except of sulfur, MBT and TMTD were prepared using Russian Banbury mixer. Its capacity is 1500 gr. Engine speed is 120 cycle/minutes. Mixing was done at 95 °C during 7 minutes approximately.

Figure 3.3 : Banbury mixer.

3.2.1.4 Two roll mill

The prepared rubber compound and rest of the ingredients were homogenized by using two-roll mill with roll dimension D=20 cm and L=50 cm with 10 rpm speed. The distance between the cylinders can be varied from 0.5 mm to 3 mm depends on the beginning or end of the mix.

Figure 3.4 : Laboratory type two roll mill.

3.2.2 Equipments used for unvulcanized rubber

3.2.2.1 Differantial scanning calorimeter (DSC)

Glass transition temperatures (T_g) and curing peak enthalpies (ΔH_c) of the compounds were obtained using a Mettler Toledo DSC1 Star System differential scanning calorimeter (DSC) according to ASTM D3418. DSC was performed to unvulcanized rubber from -80 °C to 250 °C with 10 °C/min heating rate under 1.5 bar nitrogen atmosphere.

Figure 3.5 : Differential scanning calorimeter (DSC).

3.2.2.2 Density measuring instrument

Densities of uncured compounds were calculated using Radwag density measuring instrument according to ISO 2781.

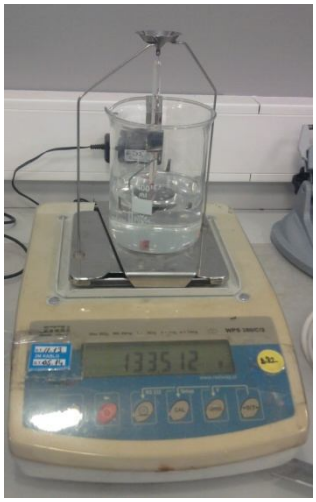

Figure 3.6 : Density measuring device.

3.2.2.3 Moving die rheometer (MDR)

Rheometric characteristics were measured using Rheometer MDR 2000, Alpha Technologies (USA) according to ISO 3417 method. Temperature were set to 160 °C and flow behaviours were examined during vulcanization such as cure time, scorch time, maximum and minimum torque etc.

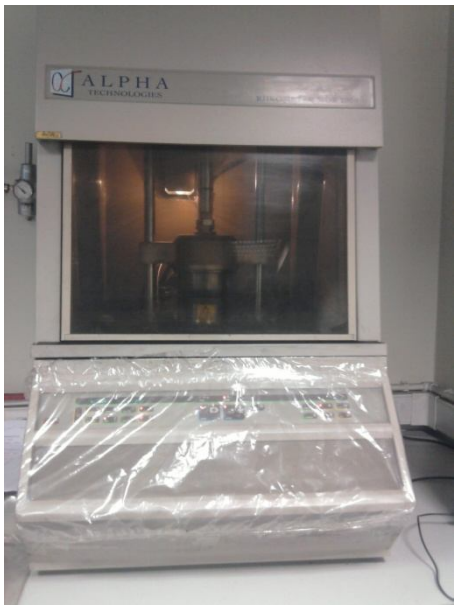

Figure 3.7 : Moving die rheometer (MDR) device.

3.2.2.4 Hot press

Uncured rubber was vulcanized and molded using Alpha Technologieshot press at a temperature of 160 °C to their respective cure times. The pressure is 220 bar. Molds are 2 mm thickness and 200 mm x200 mm dimensions for mechanical tests; 6 mm thickness and 50 mm diameters for compression set test.

Figure 3.8 : Hydraulic hot press.

3.2.2.5 Video microscopy

Morphological properties were examined using Marestek video microscope. The microscope has 250x magnification.

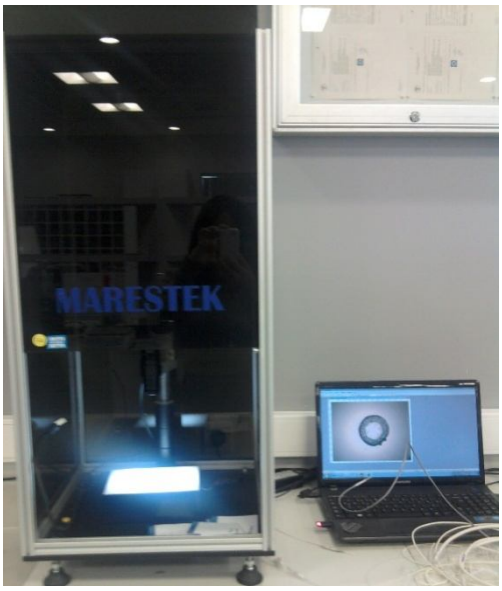

Figure 3.9 : Video microscope device.

3.2.3 Equipments used for vulcanized rubber

3.2.3.1 Universal testing machine

Tensile tests were performed using a Zwick Z0.1TH Universal Testing Machine at a speed of 500 mm/min according to DIN 53504. The machine with extensometer has 8195 pneumatic grips type and the load cell is capable of 1 kN force. Tensile strength, elongation at break, tensile modulus and tear strength were obtained from the test.

Figure 3.10 : Universal testing machine.

3.2.3.2 Hardness measuring instrument

Hardness of samples were measured by using durometer according to ASTM D2240 methods. Results are Shore A units. The error margins calculated as ±01 Shore A.

Figure 3.11 : Durometer device.

3.2.3.3 Thermogravimetric analysis (TGA)

TGA analysis was performed using a TG/DTA 7200 Exstar analyser from 20 °C to 750 °C at a heating rate of 20 °C/min under air and nitrogen atmosphere according to ASTM D6370 method.

Figure 3.12 : Thermogravimetric analyser (TGA) device.

3.3 Methods

3.3.1 Preparation of compounds

Firstly, chrome tanned leather (CTL) shavings were cutted into smaller sizes and were dried in an oven at 100 °C for 24 hours to remove the moisture. Mesh sizes of

leather particles was determined using sieve analyser. CTL was added to different mesh sizes of pans from 45 to 2000 µm and it was sifted during 10 minutes. Weights were measured in the pans and weight percentages were determined. After dried of CTL, ZnO and CT pieces were mixed and waited in the room temperature during one day. Then all rubber ingredients were accurately weighed. These all components except MBT, TMTD and sulfur were put in a banbury at 95°C during 7 minutes approximately. Paraffinic oil and CB were added to the banbury together. After mixing, the prepared compound and MBT, TMTD and sulfur were added to two roll mill. The mixing time remained constant at 5 minutes for all the compounds. Each blend was prepared 1500 grams approximately. Based on the formulations shown in Table 3.1 five different compositions of EPDM/CTL were prepared. Uncured rubber compounds were molded 2 mm and 6 mm thickness sheets in the hot press at 160 °C their respective cure times and were prepared for tests. Similarly, 5 different compositions were subject to thermal aging and same tests were done.

Table 3.1 : Compounding formulations of EPDM/CTL composites

Ingredients	phr				
EPDM	100	100	100	100	100
CTL	0	5	10	15	20
CB	100	95	90	85	80
Paraffinic oil	30	30	30	30	30
ZnO	5	5	5	5	5
Stearic acid	2	2	2	2	2
TMQ	1	1	1	1	1
IPPD	1	1	1	1	1
MBT	0.5	0.5	0.5	0.5	0.5
TMTD	0.75	0.75	0.75	0.75	0.75
Sulfur	1.5	1.5	1.5	1.5	1.5

3.3.2 Characterization of compounds

3.3.2.1 Thermal characterization

Glass transition temperatures (T_g) and curing peak enthalpies (ΔH_c) values of the uncured compounds were obtained using a differential scanning calorimeter (DSC). Analysis was done to five compounds between -80 °C to 250 °C with 10 °C/min heating rate under nitrogen gas. Pressure is 1.5 bar.

3.3.2.2 Curing characterization

Curing behaviour of compounds were obtained using Moving Die Rheometer at 160°C according to ISO 3417. Densities of uncured rubbers were measured due to obtain mass of compounds which will be moulded in hot press according to ISO 2781 method. The cure time (t_{100}), scorch time (t_{s2}), maximum torque (M_H), minimum torque (M_L), viscous torque ($S^{''}$) and tan delta values were obtained from the rheograph which can be seen in Figure 3.13. Measurement was done at least three samples from different parts of uncured rubber and average values were calculated.

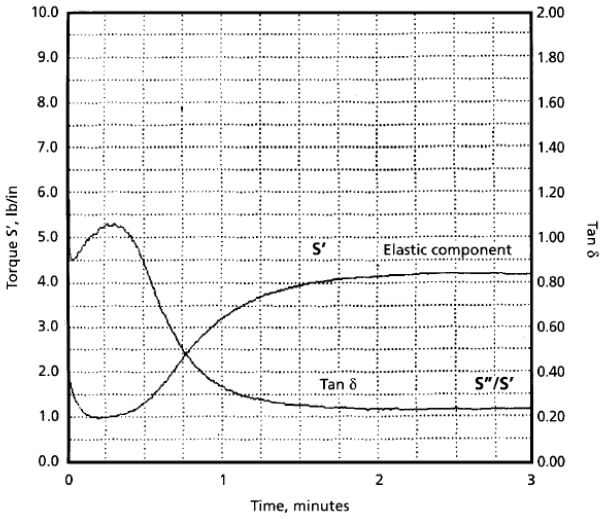

Figure 3.13 : Moving die rheometer curve.

3.3.2.3 Morphological characterization

Morphological characterization of compounds were examined using video microscope which magnification is 250x. Surface properties and distribution of leather particles in the matrix were investigated.

3.3.3 Preparation of CTL/EPDM samples

The prepared compounds were compression molded into 2 mm sheets for vulcanization at a temperature of 160 °C. Compression was done using hot press based on the t_{100} values of each compounds. Sheets were punched to prepare the dumbbell shaped specimens by cutter as seen in Figure 3.14. At least 10 specimens were prepared for each compound for mechanical tests.

Figure 3.14 : Cutter device for dumbbell shape.

3.3.4 Characterization of CTL/EPDM samples

3.3.4.1 Tensile test

Different blend ratios of compression molded sheets were investigated in terms of the mechanical properties using universal testing machine. Machine speed is 500 mm/min according to DIN 53504 method. From this test, tensile strength, elongation at break and 50% secant modulus were obtained. Specimens were dumbbell shaped as seen in Figure 3.15. At least 5 specimens were tested for each samples.

Figure 3.15 : Dumbbell shaped test pieces for tensile testing

3.3.4.2 Crosslinking densities

Crosslinking densities of samples were determined with 50% secant modulus which is obtained from tensile test. This method is easy and useful because it is really complicated to define crosslinking density from swelling measurements. E is related with CLD as in Equation (3).

$$E = 3\upsilon RT \quad \textbf{(3.1)}$$

where υ is CLD, R is universal gas constant (8.314 J mol^{-1} K^{-1}), T is absolute temperature (K).

3.3.4.3 Tear strength test

Tear strengths of different compounds were measured using universal testing machine at a speed of 200 mm/min according to ASTM D5584. Specimens thickness of 2 mm were prepared using below cutter as seen in Figure 3.16. At least 5 specimens were tested for each samples.

Figure 3.16 : Tear test pieces of rubber

3.3.4.4 Hardness test

Hardness of samples were measured using durometer. According to ASTM D2240 standards thickness of samples must be 6 mm. At least five samples were measured from different parts of the samples and averages of values were recorded as Shore A units.

3.3.4.5 Thermogravimetric analysis (TGA)

TGA analysis of the cured specimens was carried out using Exstar TGA analyser from 20 °C to 750 °C with 20 °C/min heating rate. Firstly, nitrogen gas was purged from 20 °C to 500 °C and then air was purged from 500 °C to 750 °C. Mass loss, decomposition or loss of some volatiles were observed.

3.3.5 Thermal aging characterization

Thermal aging was carried out to the vulcanized rubber samples at 70 °C 70 hours using heating oven according to ASTM D 573. After aging tensile, tear strength, hardness and compression set tests were done.

3.3.5.1 Compression set test

In compression test, rubber's ability to recover from a compressive deformation was measured. According to ASTM D395 method, 6 mm thickness and 50 mm diameter

samples were compressed at 160 °C during respective cure times. Samples were compressed by 25 % of its original thickness and it was held in this state between two steel plates during 70 °C and 70 hours for each of the five samples. The applied pressure was 40 bar. The steel plates were then removed and the thickness was re-measured. Measurements were done below device as seen in Figure 3.17.

Figure 3.17 : Compression set device.

4. RESULTS AND DISCUSSION

In this study, CTL was added to EPDM at different proportions to examine the effect of thermal, curing, mechanical and morphological properties before and after aging at 70 °C 70 hours. Five compositions were prepared according to Table 3.1. Before ingredients blended in the banbury, CTL and ZnO were mixed and waited ambient temperature during one day. After addition ZnO the state of the CTL surface undergo the change (Przepiorkowska A., Chronska K. and Zaborski M.,2007).

Particle size analyser:

Particle size distribution of CTL shavings were determined using sieve analyser. Analysis was done method which is given in the Section 3.3.1. Different mesh sizes and weight percentages of CTL particles were shown in Table 4.1.

Table 4.1 : Mesh sizes and CTL particle weights obtained from sieve analyser

Mesh size (µm)	CTL (wt.-%)
Pan	1.1
45	2.7
125	21.8
500	11.4
1000	36.6
2000	26.4

Mesh size percentages of CTL were between 45 to 2000 µm, as seen in the table. The most used particles size (36.6 wt.-%) was 1000 µm and then 2000 µm (26.4 wt.-%). Total used mesh sizes of CTL (60%) was 1000 µm and 2000 µm.

4.1 Thermal Properties of CTL/EPDM Compounds

4.1.1 Differantial scanning calorimeter (DSC)

Thermal behaviours of EPDM/CTL composites such as glass transition temperature (T_g) and curing peak enthalpies (ΔH_c) were determined using DSC devices. Analysis

was carried on between -80 to 250 °C with 10 °C/min heating rate under nitrogen gas.

The values of T_g and ΔH_c were shown in Table 4.2. As compared the values of EPDM/CTL composites, it can be seen that T_g values increased with CTL loading. The T_g of EPDM with leather samples compared to EPDM sample could be identified at higher temperature. Although the difference in T_g, that is not significant. But the increase in T_g of EPDM with leather samples are consequence of less chain mobility of rubber. The reduction of chain mobility indicates the increasing crosslinking of rubber with CTL loading.

It can be also mentioned that the curing peak enthalpies increased with loading of CTL pieces. Increasing of enthalpies shows that the crosslinking of compounds were increased from 0 to 20 phr leather adding of EPDM rubber.

Table 4.2 : T_g and curing peak enthalpies of EPDM/CTL compounds.

	T_g (°C)	ΔH_c (J/g)
EPDM	-60.1	0.9
EPDM/CTL5	-58.3	1.7
EPDM/CTL10	-58.7	2.7
EPDM/CTL15	-57.6	2.9
EPDM/CTL20	-57.8	3.3

4.2 Curing Properties of Compounds

According to ISO 2781 test method, densities of each samples were determined. Results can be seen from Table 4.3. Densities of EPDM/CTL compounds did not show significant change.

Table 4.3 : Densities of uncured EPDM/CTL samples

	Densities (g/cm^3)
EPDM	1.15
EPDM/CTL5	1.14
EPDM/CTL10	1.12
EPDM/CTL15	1.13
EPDM/CTL20	1.12

The curing characteristics of EPDM/CTL were measured using a MDR at 160 °C and from the rheograph some parameters such as scorch time, curing time, torque etc. are summarized in Table 4.4. The cure rate index was calculated from the following expression;

$$CRI = \frac{100}{t_{90} - ts_2} \quad \textbf{(4.1)}$$

where t_{90} is the optimum cure time and t_{s2} is the scorch time (Sahoo S., Maiti M., Ganguly A., George J. J. and Bhowmick A. K., 2007).

Cure extent was calculated from the following expression;

$$Cure\ extent\ (dNm) = M_H - M_L \quad \textbf{(4.2)}$$

Table 4.4 : Compounding formulation of EPDM/CTL compounds.

Composition	EPDM / CTL				
Fraction(phr)	100/0	100/5	100/10	100/15	100/20
M_L (dNm)	3.6	2.7	2.6	2.9	2.4
M_H (dNm)	13.1	11.1	10.6	12.3	12.8
t_{s2} (min)	1.4	1.3	1.3	1.4	1.5
t_{10} (min)	1.2	1.1	1.1	1.2	1.3
t_{50} (min)	2.4	2.2	2.2	2.3	2.3
t_{90} (min)	8.5	8.4	10.3	9.1	7.18
t_{100} (min)	20.9	18.8	20.8	21.0	11.5
tanδ @M_H	2.8	2.8	2.6	2.9	2.4
S" @M_H	3.6	3.1	2.7	3.5	3.1
Cure extent	9.5	8.4	8.0	9.4	10.4
CRI (min^{-1})	14.1	14.1	11.1	13.0	17.6

As observed in Table 4.4 , results show that there is a smaller amount decrease of maximum torque (M_H) values when leather particles added to EPDM as compared EPDM without leather additives. The small decreases observed for minimum torque (M_L) values as same M_H values. M_H gives information about the curative system and degree of crosslinking of the elastomer. Cure extent can give information about degree of crosslinking of the compounds due to torque values are close to each other. Cure extent increased with leather loading. Torque values versus time graphs were added to Appendix A.

If insufficient curatives are mixed to the mixer, then M_H can be low. M_L is an indirect measure of the viscosity of the compound, the decrease in the M_L found in these compositions is due to physical stiffness of the vulcanized test specimen taken

at the highest point of the curve. The difference between the maximum and minimum torque values is a measure of the dynamic shear modulus (El-Sabbagh S. H. and Mohamed O. A.,2011).

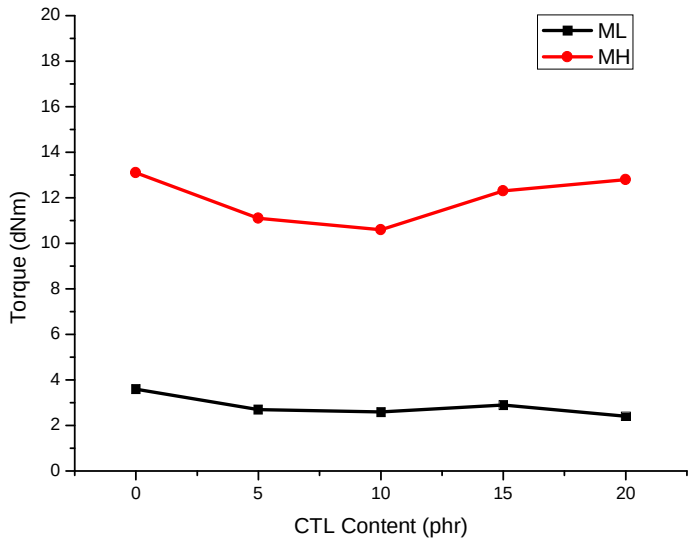

Figure 4.1 : The graph of torques of EPDM/CTL compounds.

From the rheometric parameters it follows that there is no significant change of t_{s2} and t_{50} values when leather particles added to EPDM as compared EPDM without leather additives. Scorch time (t_{s2}) is the measure of premature vulcanization and optimum cure of rubber network. Optimum cure time, t_{90} and t_{100} significantly decreased with 20 phr CTL loading. Cure rate index shows an increase, accordingly. It was observed that curing time started to decrease when CTL amounts increased a certain level.The amount of active sulfurating agents was increased with decreasing of curing time. This accelerates the formations of crosslinks and a shorter scorch time was recorded. The cure time was increased of 10 and 15 phr might be due to penetrations of EPDM matrix into the surface pores and presence of higher amounts of CTL particles which increases the free volume between rubber network resulting in prolonged vulcanization process (Ismail H. and Mathialagan M., 2011).

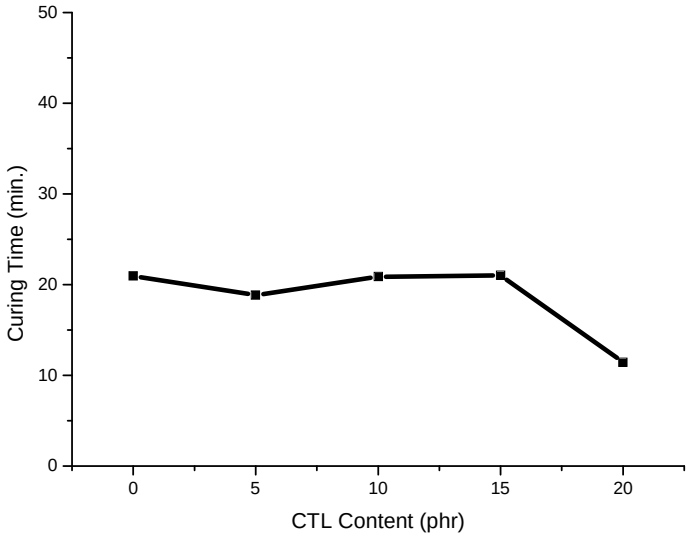

Figure 4.2 : The graph of curing time versus EPDM/CTL compounds.

The tanδ and viscous torque (S"@M_H) represent the resilience and damping properties of rubber compounds. The resilience of cured rubber compounds are greater when the tanδ value is smaller. The results obtained in Table 4.4 show that both tan δ and S" @M_H of the EPDM/CTL compounds decreased with 10 and 20 phr EPDM/CTL loading.

For compression set test, 6 mm thickness molded sheet was prepared. Curing values of these sheets (t_{100}) were determined as based on the optimum curing time of 2 mm thickness sheets. The determination is:

Curing time of 2 mm thickness sheet x 1.1 = Curing time of 6 mm thickness sheets

The results were shown in the Table 4.5.

Table 4.5 : Optimum curing time of unvulcanized rubbers at 160 ºC for compression set.

	Curing time of 6 mm sheet (min.)
EPDM	23.0
EPDM/CTL5	20.7
EPDM/CTL10	22.9
EPDM/CTL15	23.1
EPDM/CTL20	12.6

4.3 Morphological Properties of CTL/EPDM Compounds

Morphological properties of EPDM/CTL compounds was examined using video microscope with 250x magnification. Each of the leather distribution in EPDM matrix were shown in Figure 4.3. From figures it was obtained that brightness increased with addition CTL particles in EPDM rubber. It is seen that there is no agglomeration in the compounds.

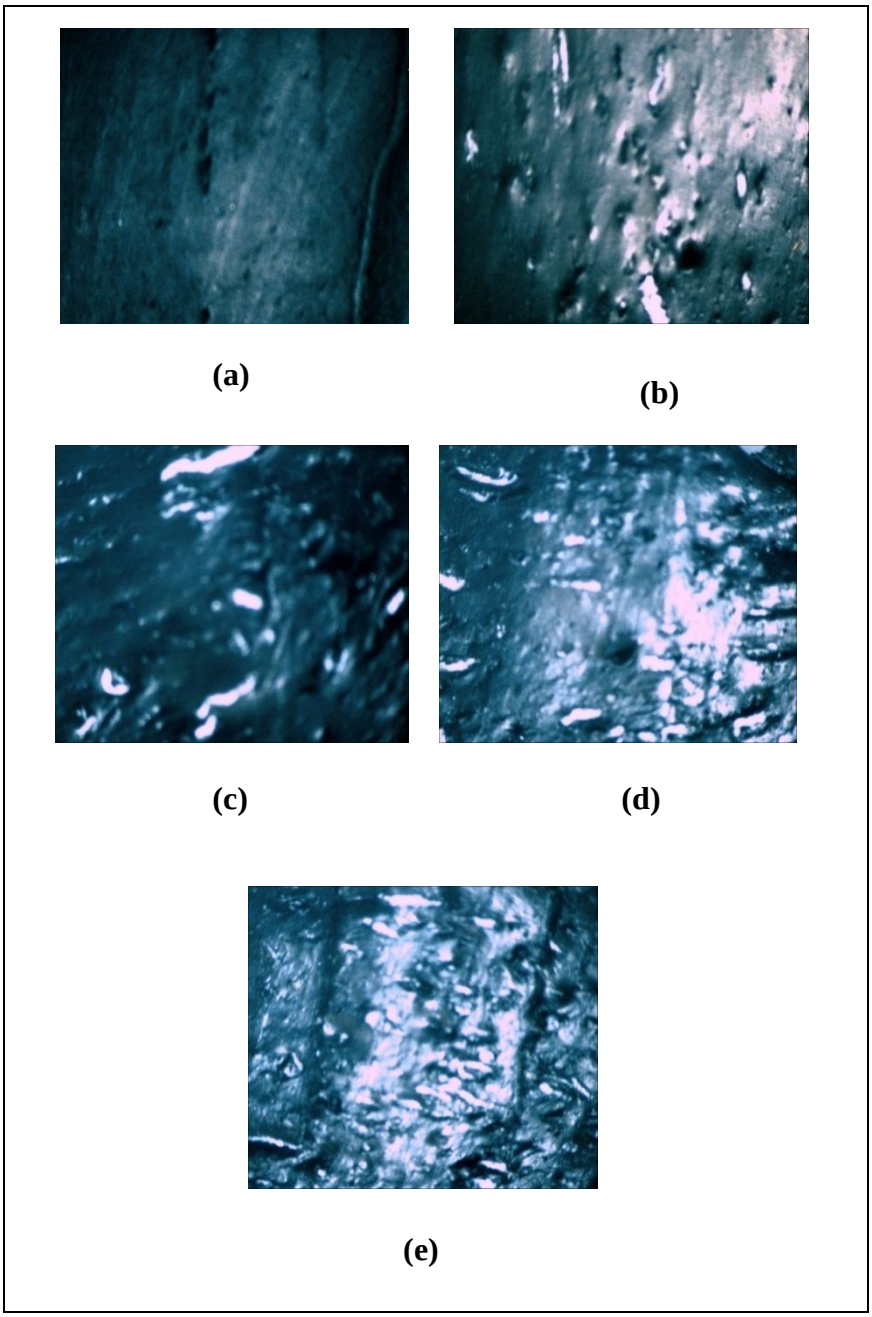

Figure 4.3 : Video microscope images of (a) EPDM, (b) EPDM/CTL5, (c) EPDM/CTL10, (d) EPDM/CTL15 and (e) EPDM/CTL20 samples.

4.4 Mechanical Properties of CTL/EPDM Samples

4.4.1 Tensile test

Tensile tests were performed at the ambient temperature using universal testing machine. Table 4.6 shows the mechanical properties of the composites as a function of leather particle loadings. At least five samples were measured from different parts of the samples and average of values was recorded.

Tablo 4.6 : Mechanical properties of EPDM/CTL samples.

	EPDM	EPDM/ CTL5	EPDM/ CTL10	EPDM/ CTL15	EPDM/ CTL20
Tensile strength (MPa)	13.2	7.7	6.9	6.9	7.1
Elongation at break (%)	247.4	237.4	233.2	219.3	186.5
50% Secant Modulus (MPa)	2.9	2.0	2.2	2.6	2.9

Figure 4.4 shows tensile strength of the composites as a function of leather particles loading 0, 5, 10, 15 and 20 phr. The addition of CTL with different ratios to EPDM rubber was decreased the tensile strength and elongation at break somewhat. This may be due to the decrease in flexibility with adding leather particles. These fillers might be restricted of EPDM chains and resulting from the increase in crosslink density and stiffness. The decrease in tensile strength and elongation at break can be attributed to the interference of leather particles as filler in EPDM chains and this causes reduction in the mobility of rubber chain. It shows that physical interaction between EPDM and CTL particles. Also a low state of cure, due to insufficient curative, as well as inadequate cure time or temperature, will also give a lowered tensile strength (Ismail H. and Mathialagan M., 2011).

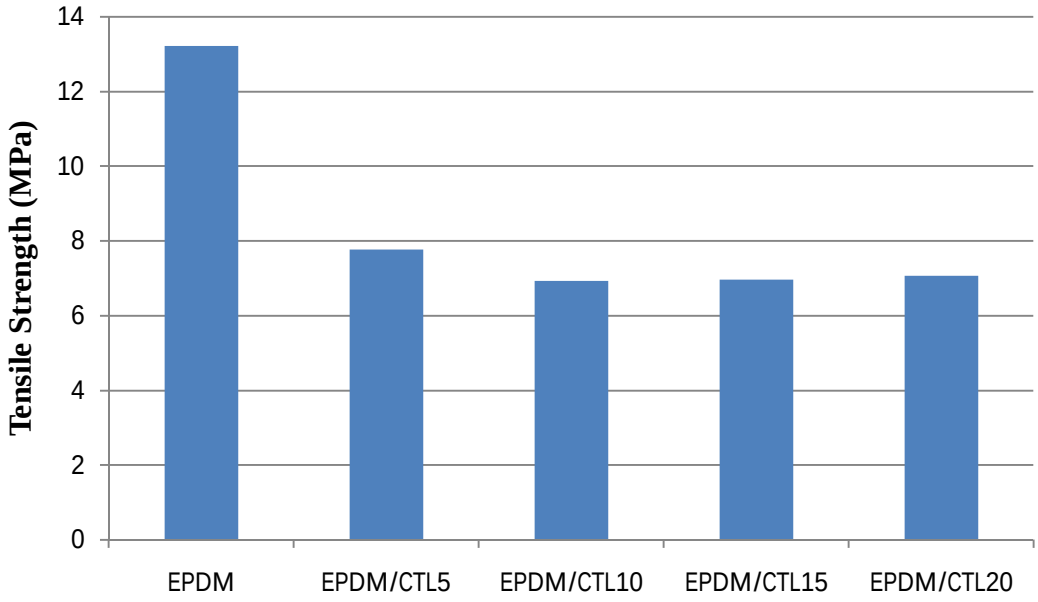

Figure 4.4 : Tensile strength of EPDM/CTL samples.

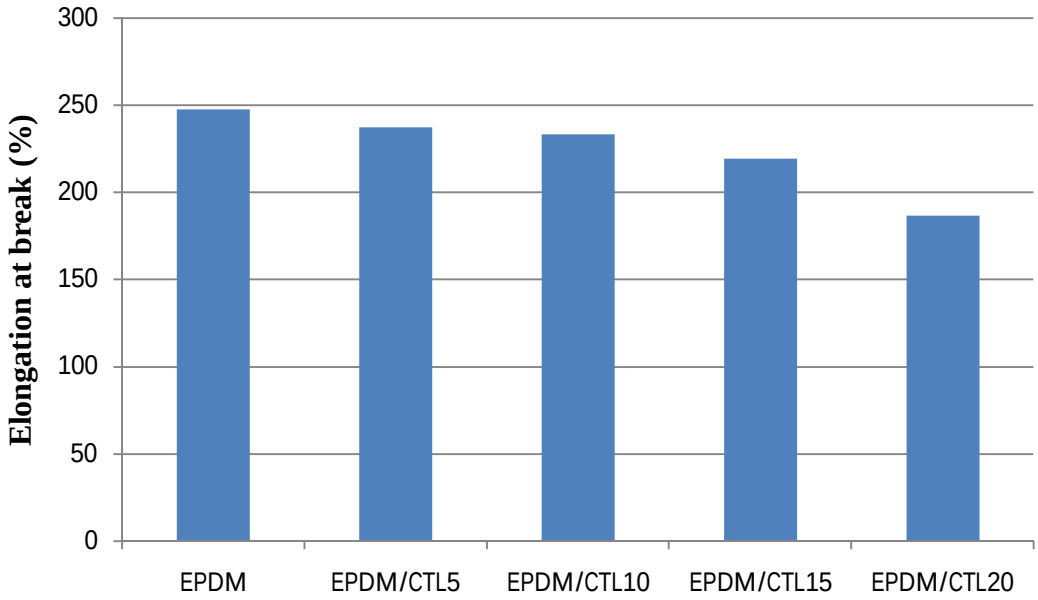

Figure 4.5 : Elongation at break of EPDM/CTL samples.

Figure 4.6 shows the effect of 50% secant modulus with CTL loading in EPDM rubber. The obtained results show that the 50% secant modulus of EPDM/CTL composite did not change significantly as compared with EPDM rubber. Modulus was decreased firstly small amount with adding 5 phr leather, but then values increased with increasing leather particles. The tensile modulus is a measure of the stiffness of the composite material and the tensile modulus depends on the filler

modulus, the amount of filler loading and the filler aspect ratio. The stiffness were increased with high modulus.

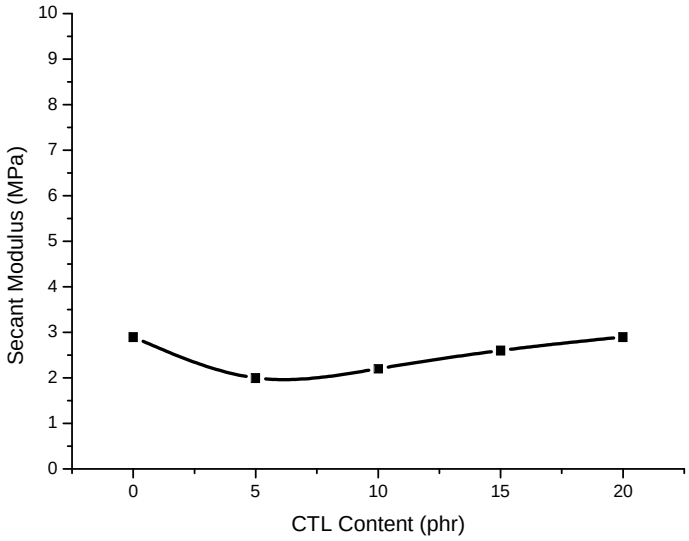

Figure 4.6 : 50% secant modulus of EPDM/CTL samples.

4.4.2 Crosslinking densities of samples

Crosslinking densities (CLD) of samples are determined according to 50% secant modulus which are obtained from tensile test. The CLD values can be seen at Table 4.7. Although crosslinking density firstly decreased with CTL addition and then increased with carry on loading. These results show that leather with first addition caused less crosslinking density, but then crosslinking density enhanced with increasing CTL particles. Results show consistent behaviour with cure extent values and also curing time.

Table 4.7 : Crosslinking densities of EPDM/CTL samples.

	Crosslinking densities (mol/m^3)
EPDM	267.6
EPDM/CTL5	187.9
EPDM/CTL10	201.8
EPDM/CTL15	246.3
EPDM/CTL20	275.9

4.4.3 Tear test

Table 4.8 shows the tear strength of EPDM/CTL composites. Tear strength were increased significantly with increasing leather particles loading from 0 to 20 phr. The increase in tear strength is due to the fibrous nature of leather that effectively prevents the growth of the test specimen crack (Ferreira M. J., Freitas F. and Almedia M. F.,2011). These increasing in tear strength is attributed to increased energy dissipation.

Table 4.8 : Tear strength of EPDM/CTL samples.

	Tear strength (N/mm)
EPDM	26.5
EPDM/CTL5	31.9
EPDM/CTL10	34.5
EPDM/CTL15	36.3
EPDM/CTL20	42.5

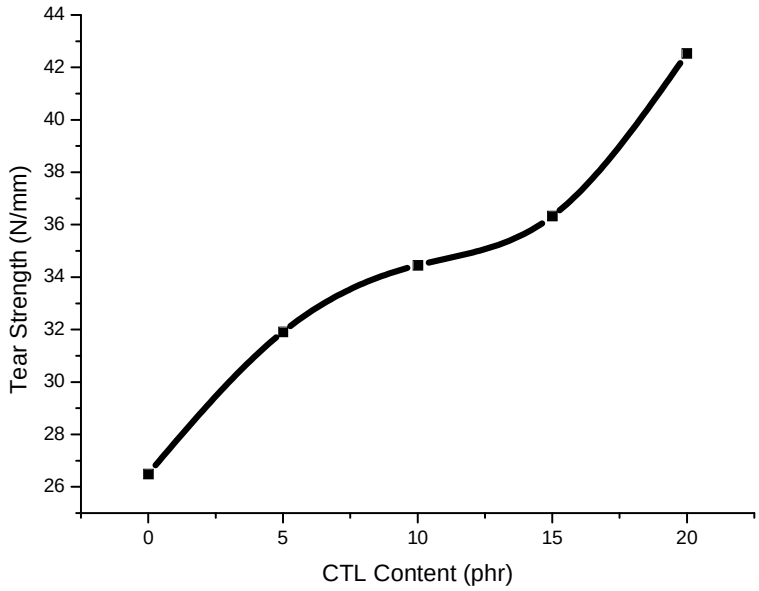

Figure 4.7 : Tear strength of EPDM/CTL samples.

4.4.4 Hardness test

Hardness increases a small amount with increasing CTL loading from 0 to 20 phr as seen from Table 4.9. These increase can be attributed to the more rigid material nature of leather particles which added higher hardness to the softer elastomer phase.

Table 4.9 : Hardness of EPDM/CTL samples.

	Hardness (Shore A)
EPDM	70
EPDM/CTL5	70
EPDM/CTL10	69
EPDM/CTL15	72
EPDM/CTL20	73

4.5 Thermal Properties of CTL/EPDM Samples

4.5.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) has been carried out to evaluate thermal behavior of samples. TGA results of the EPDM/CTL composites at different CTL loading are shown in Figure 4.8. Weight change of EPDM/CTL samples were measured with increasing temperature from 20 °C to 750 °C at a heating rate of 20 °C/min under air and nitrogen atmosphere and graph of mass loss as a function of temperature plotted.

As shown in the graph, from 0 to 200 °C, the values stayed constant for five of the samples. After 100 °C the value still stayed constant, and this shows that there is no moisture in the composites. Between 200 and 300 °C samples lost about 3% approximately.

Mass changes and the temperature of these mass changes were listed in the Table 4.10. Three significant mass loss was shown in the below table.

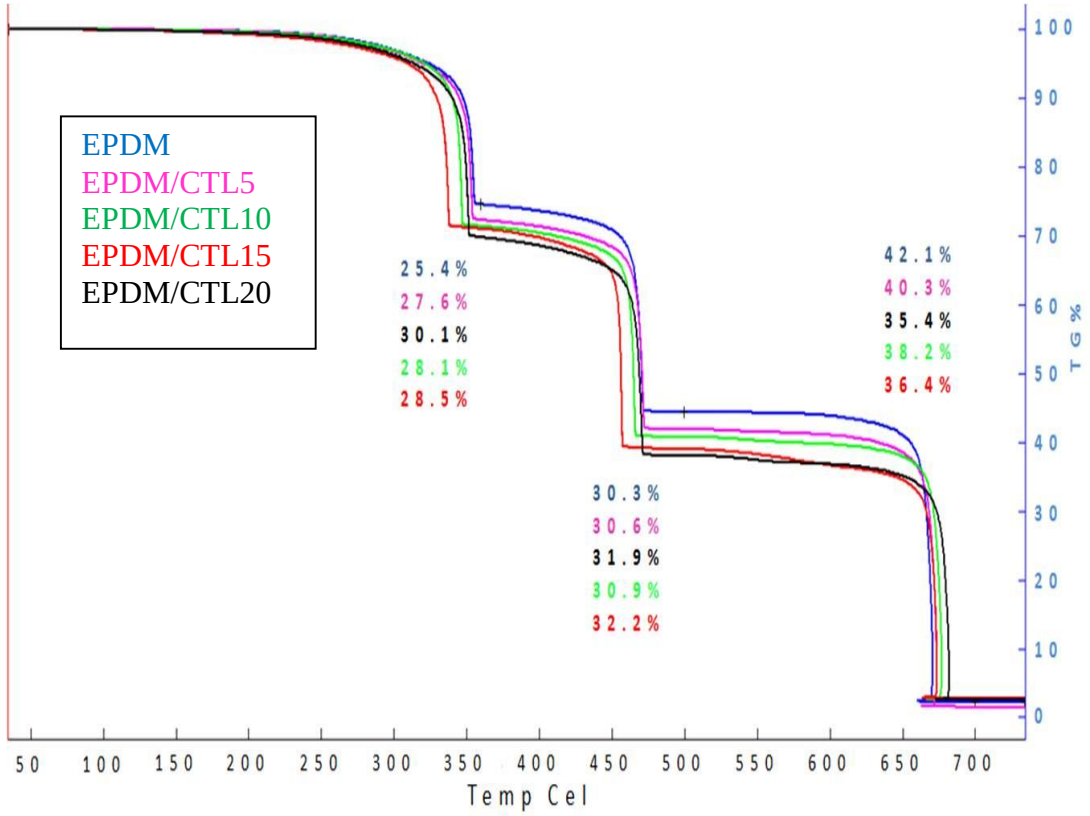

Figure 4.8 : TGA curves of EPDM/CTL samples at different CTL loading.

Between 320 °C and 350 °C first mass loss was observed in the samples. Mass loss of EPDM/CTL composites increased with increasing CTL loading. These losses can be derived from oil in the EPDM and leather particles. Same amounts of EPDM was added to all composites but CTL amounts changed. CTL includes the oil in the structure. Consequently, this increase in the composites are due to oil in the leather particles.

Table 4.10 : Mass change and temperature of EPDM and EPDM/CTL samples.

	1.mass change temp. (°C)	1. mass change (%)	2.mass change temp. (°C)	2. mass change (%)	3.mass change temp. (°C)	3. mass change (%)
EPDM	350	-25.4	450	-30.3	680	-42.1
EPDM/CTL5	350	-27.6	460	-30.6	680	-40.3
EPDM/CTL10	335	-28.4	460	-30.9	690	-38.2
EPDM/CTL15	320	-28.5	470	-32.2	690	-36.4
EPDM/CTL20	335	-30.1	470	-31.9	690	-35.4

Between 450 °C and 470 °C second mass loss was observed in the samples. Mass loss increased with increasing CTL loadings except of EPDM/CTL15 samples. These losses are due to rubber decomposition.

Between 670 °C and 690 °C third mass loss was observed in the samples. Mass loss decreased with increasing CTL loadings. These losses are due to carbon black decomposition. Carbon black amounts decreases with CTL loading and because of that CB decomposed little at high loadings as compared the smaller loadings.

The maximum weight loss of EPDM/CTL samples increased with leather loading from 0 to 20 phr. Almost 100% of samples decomposed. Approximately, 2% of samples did not decompose, stayed in the structure as inorganic filler.

4.6 Aging Properties of CTL/EPDM Samples

4.6.1 Tensile test

EPDM/CTL samples were subjected to thermal oxidating aging at 70 °C for 70 hours using a heating oven. The mechanical properties of the aged samples were measured and the results were shown in Table 4.11.

Tablo 4.11 : Mechanical properties of EPDM/CTL samples after aging at 70 °C for 70 hours.

	EPDM	EPDM/ CTL5	EPDM/ CTL10	EPDM/ CTL15	EPDM/ CTL20
Tensile strength (MPa)	13.8	7.1	7.3	6.6	5.8
Elongation at break (%)	280.5	201.3	198.1	177.0	248.9
50% Secant Modulus (MPa)	2.7	2.4	2.6	2.9	2.4

Figure 4.9 shows tensile strength of EPDM/CTL samples before and after aging. As seen from the graph, tensile strength did not show significant change with aging. Elongation at break values almost stayed constant similar to tensile strength as seen in Figure 4.10. EPDM is resistant to thermal aging because of that there is no change at tensile strength. As similar, adding of leather in EPDM showed resistance to thermal aging.

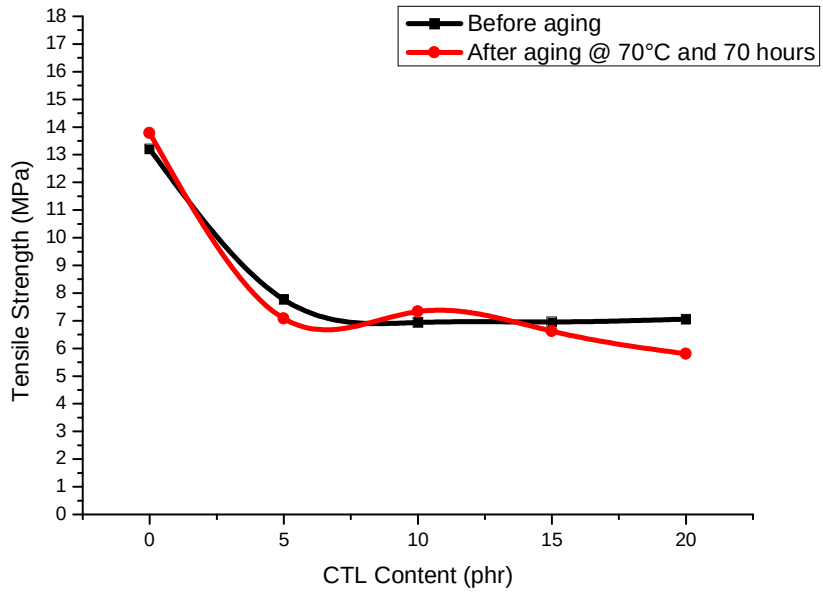

Figure 4.9 : Tensile strength of EPDM/CTL samples before and after aging at 70 °C and 70 hours.

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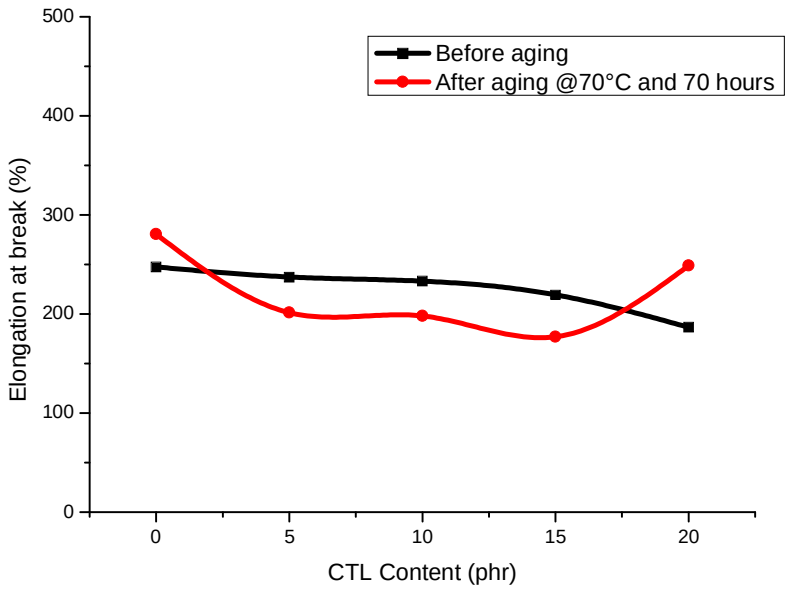

Figure 4.10 : Elongation at break of EPDM/CTL samples before and after aging at 70 °C and 70 hours.

Although there was not significant changes in the 50% secant modulus, a small increase observed after aging. The modulus is related to the crosslinking density of vulcanized rubber. The values increased due to samples subjected to heat for a while, thus curing was carried on and modulus values increased accordingly.

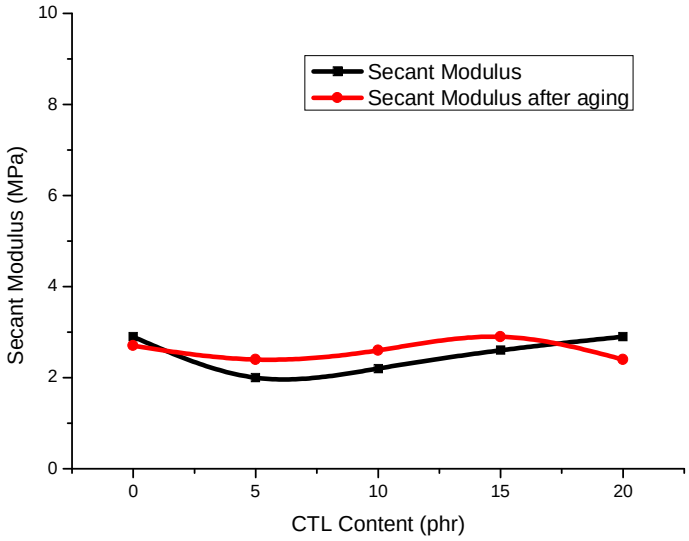

Figure 4.11 : 50% secant modulus of EPDM/CTL samples before and after aging at 70 ºC and 70 hours.

4.6.2 Tear test

Tear strength of EPDM/CTL samples after aging is shown in Table 4.12. Results showed a decrease except of EPDM rubber after aging due to its resistance to heat. The tear strength for the unaged sample is much higher than the aged ones. Energy dissipation decreased with decrasing aged samples.

Table 4.12 : Tear strength of EPDM/CTL samples.

	Tear strength (N/mm)
EPDM	26.1
EPDM/CTL5	29.6
EPDM/CTL10	30.0
EPDM/CTL15	32.2
EPDM/CTL20	33.8

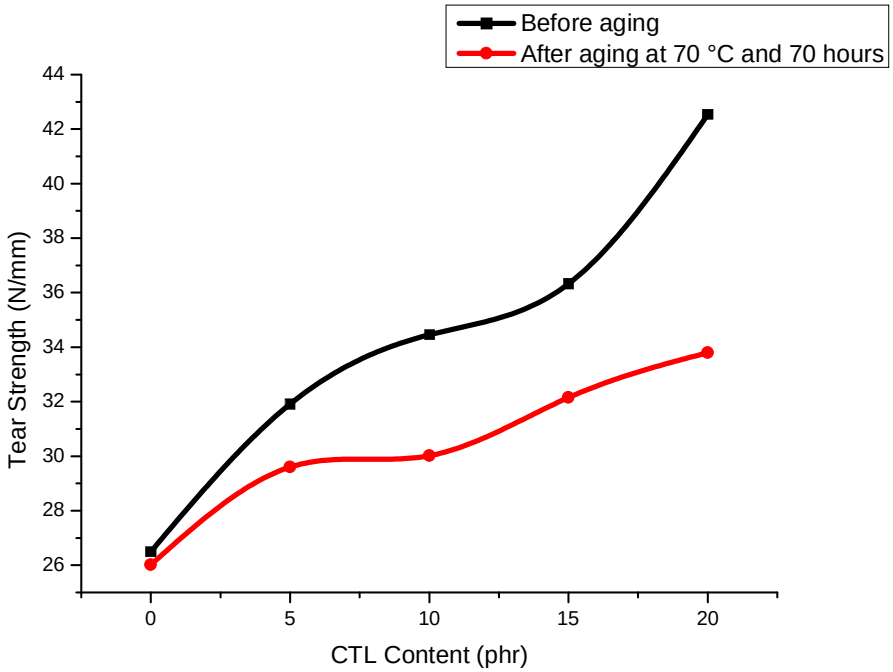

Figure 4.12 : Tear strength of EPDM/CTL samples before and after aging at 70 °C and 70 hours.

4.6.3 Hardness test

Hardness of EPDM/CTL samples after aging were recorded in Table 4.13. After aging hardness values were increased. Hardness is related to crosslink density in the structure. Similar to modulus values, due to samples subjected to heat three days curing increased and thus hardness increased accordingly. Hardness, modulus and crosslinking values showed similar effects on the samples. After aging samples became more rigid materials.

Table 4.13 : Hardness of EPDM/CTL composites after aging at 70 °C 70 hours.

	Hardness (Shore A)
EPDM	74
EPDM/CTL5	73
EPDM/CTL10	73
EPDM/CTL15	74
EPDM/CTL20	72

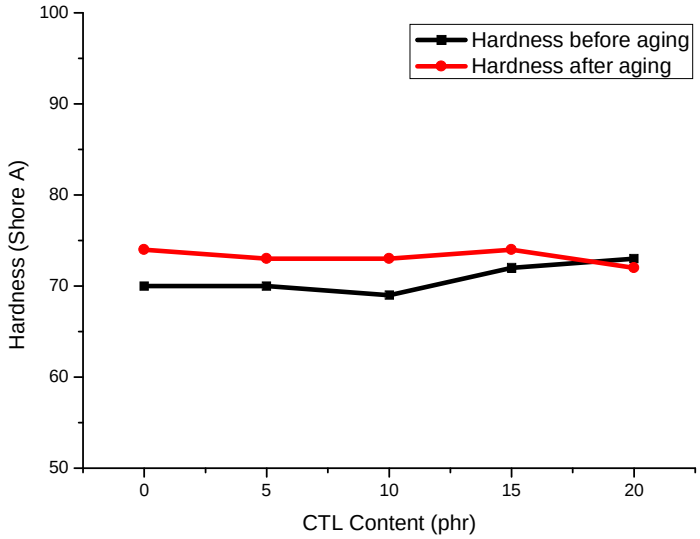

Figure 4.13 : Hardness values of EPDM/CTL samples before and after aging at 70 °C and 70 hours.

4.6.4 Compression set test

In the Figure 4.14 compression set values can be seen for each EPDM/CTL composites. Samples were compressed by 25% of its original thickness during 70 °C and 70 hours. Values increased with loading leather particles from 0 to 20 phr. Compression set measures ability of rubber to recover from a compressive deformation. If the sample recovers to its original thickness completely, it would have a zero percent compression set. If there is no recovery at all, it would have 100% compression set. Although compression set values showed no significant change, it indicated a decrease. Compressability properties of EPDM/CTL rubbers increased as compared with EPDM rubber.

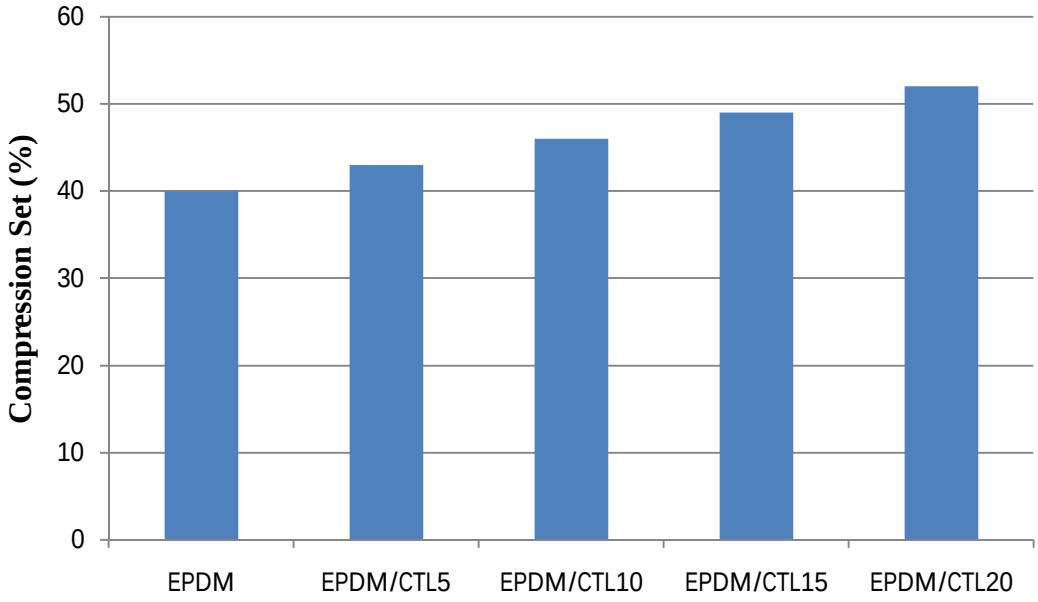

Figure 4.14 : Compression set values of EPDM/CTL composites after aging at 70 °C 70 hours.

5. CONCLUSIONS AND RECOMMENDATIONS

In this study, CTL particles were added in EPDM rubber. Mesh size percentages of leather particles were calculated between 45 to 2000 µm and the most used particle size (36.6 wt.-%) was 1000 µm. CTL particles were dried in an oven for remove moisture due to prevent any problem of compounds structure like bubble. The compounds were prepared firstly in a banbury mixer. Then accelerators were added two roll mill and mixed. This ensured the mixing was done more homogeneously. The effect of filler on compounds were investigated. After curing at 160 ºC, thermal and mechanical properties were investigated as thermal, curing and morphological properties before and after 70 ºC and 70 hours. The obtained results are summarized below.

As compared the values of EPDM/CTL samples with EPDM, it can be seen that T_g and curing peak enthalpy values increased with CTL loading. DSC curves showed that the increase in T_g of EPDM with leather samples are consequence of less chain mobility of rubber. The reduction of chain mobility indicates the increasing crosslinking of rubber with CTL loading. Densities were measured of compounds and it was shown there was not a significant change between EPDM and EPDM/CTL compounds. The curing properties show that minimum torque (M_L) and maximum torque (M_H) values showed a smaller amount decrease when leather particles added to EPDM as compared EPDM without leather additives. Torque values gives information about the curative system and degree of crosslinking of the elastomer. Cure extent can give suggestion about degree of crosslinking of the compounds due to torque values are close to each other. Cure extent increased with leather loading. Scorch time (t_{s2}) and t_{50} values did not show significant change with leather adding to EPDM. Optimum cure time, t_{90} and t_{100} significantly decreased with 20 phr CTL loading. These results were reflected to cure rate index and showed an increase, accordingly. It was observed that curing time started to decrease when CTL amounts increased a certain level. The cure time was increased with 10 and 15 phr leather adding might be due to penetrations of EPDM matrix into the surface pores and

increasing the free volume between rubber chains. The morphological properties of compounds were investigated using video microscope. Brigthness increased when leather added to EPDM. It was not observed any agglomeration in compounds.

The mechanical and thermal properties of cured samples were investigated. The addition of CTL with different ratios to EPDM rubber was decreased the tensile strength and elongation at break somewhat. These fillers were restricted of EPDM chains and resulting from the increase in crosslink density and stiffness. There was not a remarkable difference between 50% secant modulus as compared with EPDM rubber. 50% secant modulus was decreased firstly small amount with adding 5 phr leather, but then values increased with increasing leather particles. This increase means that leather wastes shows a reinforcing effect into EPDM. Also, modulus is a measure of the stiffness of samples and the modulus depends on the filler modulus, the amount of filler loading and the filler aspect ratio. The stiffness increased with high modulus. Crosslinking densities of samples are determined according to 50% secant modulus which are obtained from tensile test. Although crosslinking density firstly decreased with CTL addition and then increased with loading leather. This results showed that leather with first addition caused less crosslinking density, but then this value enhanced with increasing CTL particles. Results showed consistent behaviour with cure extent values and also curing time.The mechanical properties can be enhanced with smaller mesh sizes of leather. Tear strength were increased significantly with increasing leather particles loading from 0 to 20 phr. The increase in tear strength is due to the fibrous nature of leather and this structure effectively prevents the growth of the test specimen crack. TGA has been carried out to evaluate thermal behavior of control EPDM and rubber matrix loaded with CTL particles. The maximum weight loss of EPDM/CTL samples increased with leather waste loading from 0 to 20 phr. The curves showed three degradation step. First step was due to oil in the structure, second step was due to degradation of rubbers and the third step was due to carbon black. Almost 100% of compounds were decomposed after 750 °C temperature. Only small amount inorganic filler stayed in the samples.

The aging properties of cured samples were examined as regard to mechanical properties. Tensile strength and elongation at break did not show significant change with aging. EPDM is resistant to thermal aging and as similar, adding of leather in EPDM showed resistance to aging. Although there was not significant changes in the

50% secant modulus similarly, a small increase observed after aging. The values increased due to samples subjected to heat for a while, thus curing was carried on and modulus values increased accordingly. Hardness also showed a small increase in parallel with modulus. After aging samples became more rigid materials. Tear strength showed a small decrease except of EPDM rubber after aging. Although compression set values showed no significant change, it increased with loading leather particles from 0 to 20 phr. Compression set measures the ability of a rubber to recover from a compressive deformation. Compressability properties of EPDM/CTL increased as compared with EPDM rubber.

Consequently, adding of leather to EPDM rubber improved tear strength and compressability properties significantly, but not changing the other properties. Besides these, leather particles used as filler will reduce the cost of the final rubber product.

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APPENDICES

APPENDIX A: Torque versus time graphs

APPENDIX A

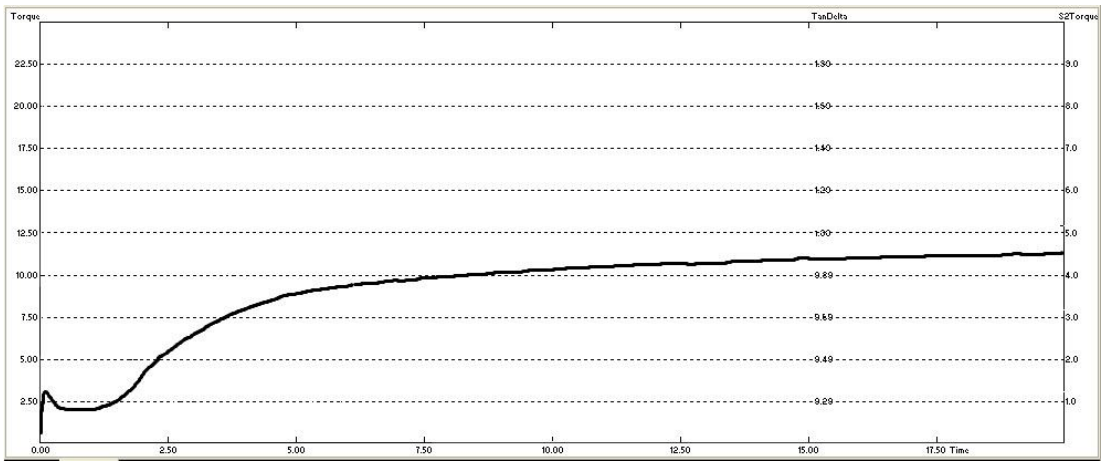

Figure A.1 : Torque versus time graph of EPDM rubber.

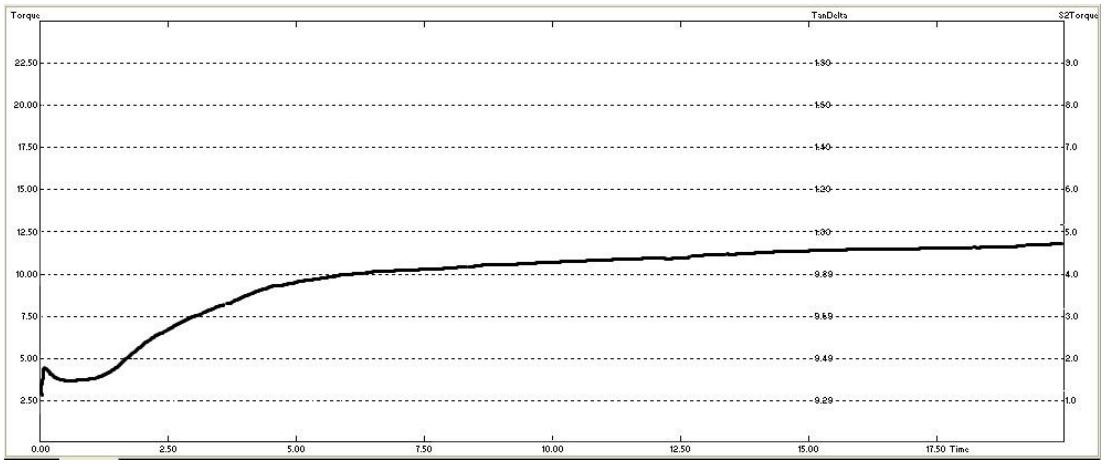

Figure A.2 : Torque versus time graph of EPDM/CTL5 sample.

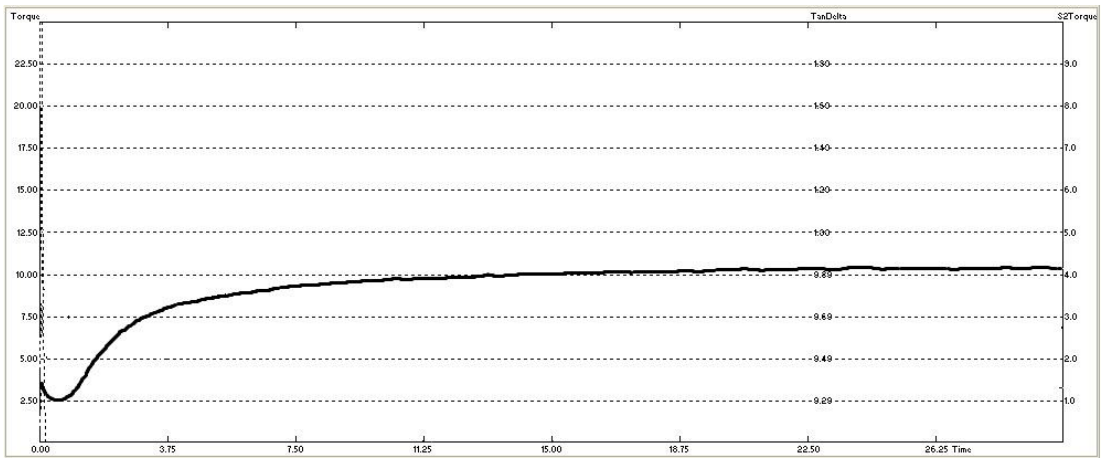

Figure A.3 : Torque versus time graph of EPDM/CTL10 sample.

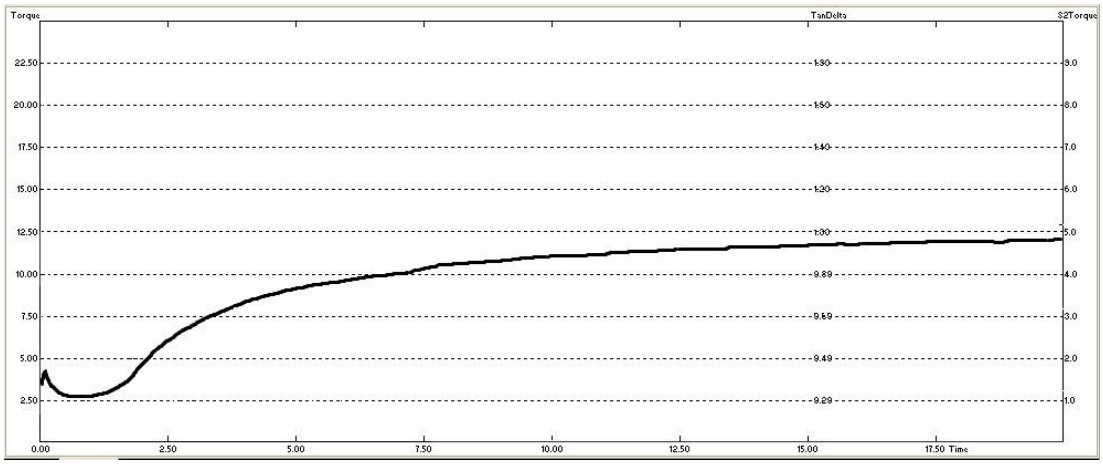

Figure A.4 : Torque versus time graph of EPDM/CTL15 sample.

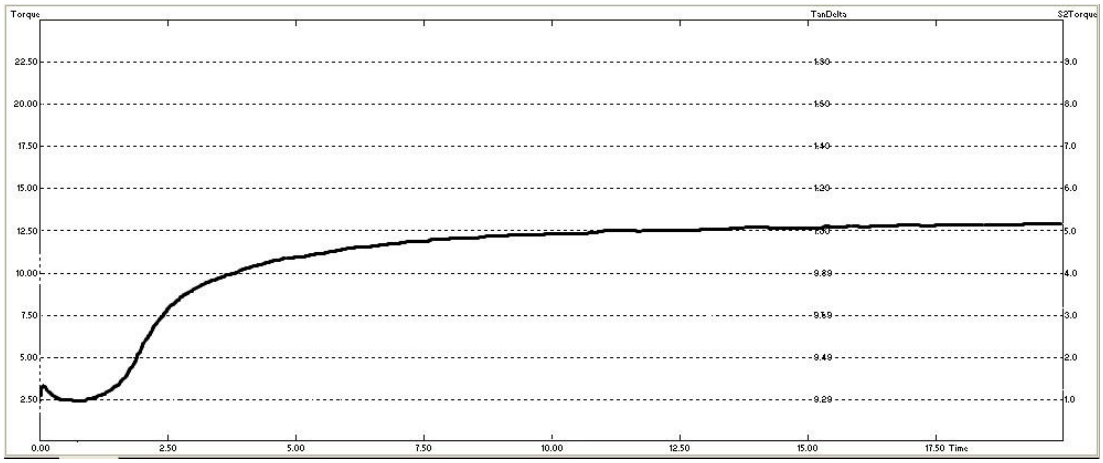

Figure A.5 : Torque versus time graph of EPDM/CTL20 sample.

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EXPERIENCES

- Meşe, P., Karaağaç, B., Uyanık, N., "Investigation of the Effects of Chrome-Tanned Leather Additives in Ethylene Propylene Diene Monomer Rubber", 2nd Rubber Conference (with international participation) organized by the Turkish Rubber Association of Turkey, 28-29 November 2014, Istanbul, Turkey (accepted).